

## DESCRIPTION

MULTI-HOLE EXTRUSION DIE, METHOD FOR PRODUCING METAL COMPOUND  
EXTRUSION-MOLDED BODY, METHOD FOR PRODUCING CATALYST  
5 EXTRUSION-MOLDED BODY FOR PRODUCTION OF UNSATURATED ALDEHYDE  
AND/OR UNSATURATED CARBOXYLIC ACID, AND METHOD FOR PRODUCING  
UNSATURATED ALDEHYDE AND/OR UNSATURATED CARBOXYLIC ACID

### TECHNICAL FIELD

10 [0001]

The present invention relates to a multi-hole extrusion die, a method for producing metal compound extrusion-molded bodies, a method for producing catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, and a method for producing an unsaturated aldehyde and/or unsaturated carboxylic acid.

15

### BACKGROUND ART

[0002]

Many methods have been proposed for producing a catalyst for use in production of an unsaturated aldehyde and/or unsaturated carboxylic acid through gas-phase catalytic oxidation of  
20 a raw material. Examples of the method proposed include a method in which an organic compound, such as alcohol, is added in kneading a catalyst component (Patent Literatures 1 and 2), a method in which a catalyst is formed through extrusion molding followed by freezing (Patent Literature 3), and a method in which a catalyst is formed through two-step extrusion molding (Patent Literature 4).

25

### PRIOR ART LITERATURE

Patent Literature

[0003]

Patent Literature 1: JP H05-309273 A

30 Patent Literature 2: JP H06-15178 A

Patent Literature 3: JP H05-309274 A

Patent Literature 4: JP 2003-093882 A

### SUMMARY OF INVENTION

## PROBLEMS TO BE SOLVED BY THE INVENTION

[0004]

However, the catalyst obtained by using any of these methods is insufficient as a catalyst for industrial use in terms of catalyst performance such as catalytic activity and selectivity for an intended product. In addition, each of these methods is insufficient with respect to the yield in catalyst production. Accordingly, from an industrial point of view, further improvement is desired for a method for producing catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, and is desired for an extrusion die for use in the method.

[0005]

An object of the present invention is to provide a multi-hole extrusion die which enables production of catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance.

## MEANS FOR SOLVING PROBLEMS

[0006]

The present invention is the following [1] to [15].

[0007]

[1] A multi-hole extrusion die including:

a die body including die holes and a flow adjuster that allows a material to be molded to evenly flow into the die holes; and

a breaker plate including a material having a proof stress of 300 MPa or higher, the breaker plate being provided with a plurality of through-holes each having a size of a (mm), and the breaker plate having a thickness of b (mm), wherein

b/a is 0.5 or more and less than 3.0, and

the multi-hole extrusion die has a structure in which a center section of the breaker plate is supported on a flat section provided to the flow adjuster of the die body.

[0008]

[2] A method for producing metal compound extrusion-molded bodies, including a step of extrusion-molding a kneaded product of a metal compound by using the multi-hole extrusion die according to [1] to produce metal compound extrusion-molded bodies.

[0009]

[3] The method for producing metal compound extrusion-molded bodies according to

[2], wherein the metal compound is a metal compound catalyst.

[0010]

[4] The method for producing metal compound extrusion-molded bodies according to [3], wherein the metal compound catalyst contains molybdenum.

5 [0011]

[5] The method for producing metal compound extrusion-molded bodies according to any one of [2] to [4], wherein the multi-hole extrusion die includes a material that does not reduce the kneaded product.

[0012]

10 [6] The method for producing metal compound extrusion-molded bodies according to any one of [2] to [5], wherein the breaker plate includes at least one stainless steel material selected from the group consisting of martensitic stainless steel material, duplex stainless steel material, and precipitation-hardening stainless steel material.

[0013]

15 [7] The method for producing metal compound extrusion-molded bodies according to any one of [2] to [6], wherein a member other than the breaker plate in the multi-hole extrusion die includes at least one stainless steel material selected from the group consisting of austenitic stainless steel material, martensitic stainless steel material, ferritic stainless steel material, duplex stainless steel material, precipitation-hardening stainless steel material, and superalloy.

20 [0014]

[8] The method for producing metal compound extrusion-molded bodies according to any one of [2] to [7], wherein extrusion pressure applied to the kneaded product in the extrusion-molding of the kneaded product by using the multi-hole extrusion die is 0.1 to 30 MPaG.

25 [0015]

[9] A method for producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid, including a step of extrusion-molding a kneaded product of a catalyst for production of acrolein and acrylic acid by using the multi-hole extrusion die according to [1], wherein

30 the catalyst extrusion-molded bodies for production of acrolein and acrylic acid are for use in production of acrolein and acrylic acid through gas-phase catalytic oxidation of propylene with molecular oxygen, and at least contain molybdenum and bismuth.

[0016]

[10] A method for producing catalyst extrusion-molded bodies for production of

methacrolein and methacrylic acid, including a step of extrusion-molding a kneaded product of a catalyst for production of methacrolein and methacrylic acid by using the multi-hole extrusion die according to [1], wherein

the catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid are for use in production of methacrolein and methacrylic acid through gas-phase catalytic oxidation of isobutylene and/or tertiary butyl alcohol with molecular oxygen, and at least contain molybdenum and bismuth.

[0017]

[11] A method for producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid, including a step of extrusion-molding a kneaded product of a catalyst for production of an unsaturated carboxylic acid by using the multi-hole extrusion die according to [1], wherein

the catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid are for use in production of the unsaturated carboxylic acid through gas-phase catalytic oxidation of an unsaturated aldehyde with molecular oxygen, and contain molybdenum and contains phosphorous and/or vanadium.

[0018]

[12] The method for producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid according to [11], wherein the unsaturated aldehyde is (meth)acrolein, and the unsaturated carboxylic acid is (meth)acrylic acid.

[0019]

[13] A method for producing acrolein and acrylic acid, including:

a step of producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid by using the method according to [9]; and

a step of filling a reactor with the extrusion-molded bodies and subjecting propylene to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[0020]

[14] A method for producing methacrolein and methacrylic acid, including:

a step of producing catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid by using the method according to [10]; and

a step of filling a reactor with the extrusion-molded bodies and subjecting isobutylene and/or tertiary butyl alcohol to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[0021]

[15] A method for producing an unsaturated carboxylic acid, including:

a step of producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid by using the method according to [11] or [12]; and

5 a step of filling a reactor with the extrusion-molded bodies and subjecting the unsaturated aldehyde to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

## EFFECTS OF THE INVENTION

[0022]

10 The multi-hole extrusion die according to the present invention enables production of catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance.

## 15 BRIEF DESCRIPTION OF DRAWINGS

[0023]

[Figure 1] Figure 1 is a cross-sectional view illustrating an example of the multi-hole extrusion die according to the present invention.

[Figure 2] Figure 2 is a cross-sectional view illustrating a multi-hole extrusion die used in  
20 Comparative Example 1.

[Figure 3] Figure 3 is a cross-sectional view illustrating a multi-hole extrusion die used in Comparative Examples 2 and 6.

[Figure 4] Figure 4 is a top view illustrating an example of the arrangement of the through-holes of the breaker plate according to the present invention.

25

## MODE FOR CARRYING OUT THE INVENTION

[0024]

[Multi-hole extrusion die]

30 The multi-hole extrusion die according to the present invention includes a die body including die holes and a flow adjuster that allows a material to be molded to evenly flow into the die holes; and a breaker plate including a material having a proof stress of 300 MPa or higher, the breaker plate being provided with a plurality of through-holes each having a size of "a (mm)", and the breaker plate having a thickness of "b (mm)". Here, b/a is 0.5 or more and less than 3.0. The multi-hole extrusion die has a structure in which a center section of the breaker plate is

supported on a flat section provided to the flow adjuster of the die body. Through producing catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid by using a method described later with the multi-hole extrusion die, catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance, can be produced at a high yield without causing deformation, breakage, or the like of the apparatus. Thus, it is preferable that the multi-hole extrusion die be a multi-hole extrusion die for producing catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid.

[0025]

Figure 1 illustrates an example of the multi-hole extrusion die according to the present invention. The multi-hole extrusion die illustrated in Figure 1 is composed of a die body 1 including die holes 6 and a flow adjuster 3 that allows a material to be molded to evenly flow into the die holes 6; and a breaker plate 4. A tip of the flow adjuster 3 of the die body 1, the tip facing to the breaker plate 4, is flat, and a center section of the breaker plate 4 is supported on the flat section of the tip. A material to be extrusion-molded which is disposed in a cylinder 2 is pushed by a piston head 5, and extruded from the die holes 6 of the die body 1 via through-holes 7 of the breaker plate 4, and thus molded.

[0026]

The arrangement pattern of the die holes of the die body can be arbitrarily selected from a concentric circle pattern (single or multiple), a grid pattern, a staggered pattern, and so on. However, a concentric circle pattern (single) is preferred from the viewpoint of uniform differential pressures at the die holes. The number of the die holes of the die body is preferably 2 to 50, more preferably 5 to 30, and even more preferably 10 to 25, though the number of the die holes is not limited thereto. The configuration with two or more die holes provides enhanced productivity for a molded article. The configuration with 50 or less die holes can provide uniform differential pressures at the die holes, while a die size allowing easy handling is maintained. The size of each die hole is preferably 2 to 10 mm, and more preferably 3 to 7 mm. The configuration with die holes each having a size of 2 mm or larger can provide reduced differential pressures when reaction is performed. The configuration with die holes each having a size of 10 mm or smaller can prevent lower catalyst performance caused by lower heat transfer performance and by lower diffusion performance in the pores inside the catalyst. The term "size" as used in the present invention refers to the maximum distance across a hole, and represents a diameter in the case that the hole is circular, and a diagonal length in the case that

the hole is rectangular.

[0027]

A breaker plate is installed in the multi-hole extrusion die according to the present invention. A breaker plate is a perforated plate for use in extrusion molding. The breaker plate according to the present invention includes a plurality of through-holes. In the case of an orifice plate with a single hole, uniform differential pressures at the die holes cannot be achieved. The pattern of the through-holes of the breaker plate can be arbitrarily selected from a radial pattern, a concentric circle pattern, a grid pattern, a staggered pattern, and so on. However, a radial pattern as illustrated in Figure 4 is preferred because a higher aperture ratio can be achieved.

[0028]

When the size of through-holes of the breaker plate is represented by "a (mm)" and the thickness of the breaker plate by "b (mm)",  $b/a$  is 0.5 or more and less than 3.0, preferably 0.7 or more and 2.7 or less, more preferably 1.0 or more and 2.5 or less, and even more preferably 1.3 or more and 2.0 or less. If  $b/a$  is less than 0.5, the breaker plate cannot endure extrusion pressure, and is deformed. Also, a foreign matter passes through the breaker plate to cause blocking of the die holes. In addition, uniform differential pressures are generated at the die holes, which causes not only larger unevenness in lengths of extrusion-molded bodies at the die holes, but also larger variation of pore distribution in the inside of catalyst extrusion-molded bodies, leading to lower catalyst performance. If  $b/a$  is 3.0 or more, deformation of the breaker plate due to large differential pressure and clogging of the breaker plate are caused. Also, strong shear is generated in a material to be molded, and particles constituting catalyst extrusion-molded bodies are broken by the strong shear to decrease the pores in the inside of the catalyst, leading to lower catalyst performance.

[0029]

The size of through-holes of the breaker plate, a, is preferably 2 to 10 mm, more preferably 3 to 8 mm, even more preferably 4 to 6 mm, and particularly preferably identical to the size of the die holes. The configuration with through-holes each having a size, a, of 2 mm or larger can prevent deformation of the breaker plate due to large differential pressure and clogging of the breaker plate. In addition, lowering of catalyst performance can be prevented, the lowering being due to the phenomenon that strong shear is generated in a material to be molded, and particles constituting catalyst extrusion-molded bodies are broken by the strong shear to decrease the pores in the inside of the catalyst. The configuration with through-holes each having a size, a, of 10 mm or smaller provides uniform differential pressures at the die

holes, which provides not only smaller unevenness in lengths of extrusion-molded bodies at the die holes, but also smaller variation of pore distribution in the inside of catalyst extrusion-molded bodies, leading to enhanced catalyst performance. If the size of through-holes,  $a$ , is set smaller than the size of the die holes, the phenomenon that a foreign matter passes through the breaker plate to cause blocking of the die holes can be prevented. For the size of the through-holes,  $a$ , a single value may be used, or alternatively, two or more sizes may be used in combination. In the case that two or more sizes are used in combination, the size of through-holes,  $a$ , represents the mean of the sizes of the through-holes.

[0030]

The thickness of the breaker plate,  $b$ , is preferably 3 to 20 mm, more preferably 4 to 15 mm, even more preferably 5 to 10 mm, and particularly preferably 6 to 9 mm. The configuration with a breaker plate having a thickness,  $b$ , of 3 mm or larger can prevent deformation of the breaker plate. The configuration with a breaker plate having a thickness,  $b$ , of 20 mm or smaller can prevent lowering of catalyst performance, the lowering being due to the phenomenon that strong shear is generated in the breaker plate, and particles constituting catalyst extrusion-molded bodies are broken by the strong shear to decrease the pores in the inside of the catalyst.

[0031]

The aperture ratio of the breaker plate (the ratio of the total area of the aperture portions of the through-holes to the cross-sectional area of a cylinder of an extruder calculated from the cylinder diameter of the extruder) is preferably 10 to 50%, more preferably 20 to 45%, and even more preferably 30 to 40%. The configuration such that the aperture ratio is 10% or higher can prevent deformation of the breaker plate due to large differential pressure and clogging of the breaker plate. In addition, lowering of catalyst performance can be prevented, the lowering being due to the phenomenon that strong shear is generated in a material to be molded, and particles constituting extrusion-molded bodies are broken by the strong shear to decrease the pores in the inside of the catalyst. The configuration such that the aperture ratio is 50% or lower ensures the strength of the breaker plate, and the breaker plate is prevented from being deformed or rupturing.

[0032]

The breaker plate includes a material having a proof stress of 300 MPa or higher. Here, proof stress means a limit of a stress value at which a material does not undergo plastic deformation. Proof stress is measured in accordance with a method set forth in JIS Z 2241:2011. The proof stress of the material is preferably 500 MPa or higher, more preferably

700 MPa or higher, and even more preferably 1000 MPa or higher. The upper limit of the range of the proof stress of the material is not limited, and can be, for example, 2000 MPa or lower. The configuration such that the proof stress of the material is 300 MPa or higher not only prevents plastic deformation or rupture of the breaker plate, but also can inhibit the phenomenon that the plastic deformation or rupture causes ununiform flowing status in the die to cause larger unevenness in lengths of extrusion-molded bodies at the die holes. This results in smaller variation of pore distribution in the inside of catalyst extrusion-molded bodies, leading to enhanced catalyst performance. For example, a catalyst for production of methacrylic acid through gas-phase catalytic oxidation of methacrolein contains an easily-reducible metal compound. Accordingly, when extrusion-molded bodies are produced by using a kneaded product containing an easily-reducible metal compound, it is preferable for the breaker plate to include a material that does not reduce the kneaded product, described later, containing a metal compound, from the viewpoint of preventing the kneaded product from being reduced.

[0033]

Examples of the material having a proof stress of 300 MPa or higher include stainless steel materials including martensitic stainless steel material (SUS403, SUS410, SUS410J1, SUS416, SUS420J1, SUS420J2, SUS431, SUS440C), duplex stainless steel material (SUS329J1, SUS329J3L, SUS329J4L, S32750, S32750), and precipitation-hardening stainless steel material (SUS630S, SUS630H900, SUS630H1025, SUS630H1075, SUS630H1150, SUS631S, SUS631TH1050, SUS631RH950). Each of these stainless steel materials also corresponds to the above-described material that does not reduce the kneaded product. One of these stainless steel materials may be used, or two or more thereof may be used in combination. The surface of the breaker plate may be subjected to electroless plating or electroplating for the purpose of inhibiting reduction of extrusion-molded bodies. Heat-treated high-speed steel or die steel may be additionally used for the surface of the breaker plate for the purpose of enhancing the proof stress. However, it is preferable to use any of the above stainless steel materials in view of abrasion or the like of a material of the surface of the breaker plate.

[0034]

The content of the material having a proof stress of 300 MPa or higher in the breaker plate is preferably 80% by mass or more, more preferably 90% by mass or more, and particularly preferably 100% by mass or more, in other words, it is particularly preferable that the breaker plate consists of the material having a proof stress of 300 MPa or higher.

[0035]

The multi-hole extrusion die according to the present invention has a structure in which

a center section of the breaker plate is supported on a flat section provided to the flow adjuster of the die body. Specifically, a center section of the breaker plate is supported on the surface of a flat section of a tip of the flow adjuster, where the tip is composed of a flat surface. In the present invention, the configuration such that the tip of the flow adjuster of the die body, the tip facing to the breaker plate, is flat allows the breaker plate to be stably supported on the surface of the flat section and the deformation thereof can be prevented. In particular, it is preferable that the flow adjuster of the die body according to the present invention have the shape of a truncated cone. It is preferable that no through-hole be provided in a portion of the breaker plate in contact with the flat section of the flow adjuster. Such a configuration imparts increased strength to the breaker plate, and deformation of the breaker plate can be more reliably prevented.

[0036]

The area of the portion of the breaker plate in contact with the flat section of the flow adjuster is preferably 0.5 to 10%, more preferably 1 to 5%, and even more preferably 2 to 4% of the area of the flat section of the breaker plate (the cross-sectional area of a cylinder of an extruder calculated from the cylinder diameter of the extruder). By virtue of the configuration such that the ratio of the area is 0.5% or more, the stress at the portion in contact with the flow adjuster is lower, and as a result deformation of the breaker plate can be prevented. By virtue of the configuration such that the ratio of the area is 10% or less, the effective area of the breaker plate is larger, and as a result enhanced processing efficiency is provided.

[0037]

The flow adjuster of the die body and the breaker plate may be only contacting with each other without being integrated, or may be integrated through fixing the flat section of the flow adjuster and the breaker plate together by using bolts. In the case that the flow adjuster has the shape of a truncated cone, assuming that the truncated cone is a cone, the angle of the cone is preferably 30 to 150°, more preferably 70 to 130°, and even more preferably 100 to 120°. The configuration such that the angle of the cone is within the above-mentioned range provides enhanced flow-adjusting effect to result in smaller unevenness in lengths of extrusion-molded bodies at the die holes.

[0038]

As described later, the multi-hole extrusion die according to the present invention is used when a kneaded product of a metal compound is extrusion-molded in a method for producing metal compound extrusion-molded bodies, the method including a step of extrusion-molding a kneaded product of a metal compound to produce metal compound

extrusion-molded bodies. Here, it is preferable for the multi-hole extrusion die to include a material that does not reduce the kneaded product, from the viewpoint of enhancement of catalyst performance and prevention of the oxidation corrosion and cracking of the multi-hole extrusion die. The "kneaded product" corresponds, for example, to a kneaded product  
5 containing particles containing a catalyst component, and to a primary molded body thereof in a method for producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid, which will be described later.

[0039]

Examples of the material that does not reduce the kneaded product for the breaker plate  
10 include the above-mentioned stainless steel materials. Examples of the material that does not reduce the kneaded product for a member, other than the breaker plate, used in multi-hole extrusion die include stainless steel materials including austenitic stainless steel material (SUS201, SUS202, SUS301, SUS302, SUS303, SUS303Se, SUS304, SUS304N1, SUS304N2, SUS304LN, SUS305, SUS309S, SUS310S, SUS316, SUS316H, SUS316L, SUS316N,  
15 SUS316LN, SUS316J1, SUS316J1L, SUS317, SUS317L, SUS317J1, SUS321, SUS321H, SUS347, SUS347H, SUSXM7, SUSXM15J1, QS2025MT, QS2025MC, QX5), martensitic stainless steel material (SUS403, SUS410, SUS410J1, SUS416, SUS420J1, SUS420J2, SUS431, SUS440C), ferritic stainless steel material (SUS405, SUS410L, SUS430, SUS430F, SUS434, QS192, QS261, SIC9, SIC10, SIC12), duplex stainless steel material (SUS329J1, SUS329J3L,  
20 SUS329J4L, S32750), precipitation-hardening stainless steel material (SUS630S, SUS630H900, SUS630H1025, SUS630H1075, SUS630H1150, SUS631S, SUS631TH1050, SUS631RH950), and superalloy (NCF600, NCF601, NCF800, NCF800H, NCF825, QA400, Ni200, Ni201). One of them may be used, or two or more of them may be used in combination. An electroless-plated or electroplated SS material, high-speed steel, die steel, or the like may be used  
25 for the surface of a member for the purpose of inhibiting reduction of the kneaded product by the surface of the member. However, it is preferable to use any of the above stainless steel materials in view of abrasion or the like of the surface of a member.

[0040]

When extrusion molding is performed by using the multi-hole extrusion die according  
30 to the present invention, the extrusion pressure in the primary side of the breaker plate is preferably 0.1 to 30 MPaG, more preferably 0.5 to 20 MPaG, even more preferably 1.0 to 15 MPaG, and particularly preferably 2.0 to 13 MPaG. By virtue of the extrusion pressure of 0.1 MPaG or higher, sufficient differential pressures are generated at the die holes to result in smaller unevenness in lengths of extrusion-molded bodies at the die holes. By virtue of the extrusion

pressure of 30 MPaG or lower, lowering of catalyst performance can be prevented, the lowering being due to the phenomenon that strong shear is generated at the breaker plate or die holes, and particles constituting catalyst extrusion-molded bodies are broken by the strong shear to decrease the pores in the inside of the catalyst.

5 [0041]

Molded bodies extruded from the multi-hole extrusion die are cut into pieces of any size, and the length of molded bodies after being cut is preferably 2 to 10 mm, and more preferably 3 to 7 mm. By virtue of the length of 2 mm or larger, pressure loss in a reactor filled therewith can be lowered. By virtue of the length of 10 mm or smaller, lowering of catalyst performance  
10 can be prevented, the lowering being accompanied by lowering of diffusion in pores in the inside of a catalyst and heat transfer performance. Any cutting method can be selected, and examples thereof include a method of using a cutting blade which rotates around a center section of a die surface as a rotational axis, and a method of using a cutting blade reciprocating in parallel with a die surface.

15 [0042]

[Method for producing metal compound extrusion-molded bodies]

The method according to the present invention for producing metal compound extrusion-molded bodies includes a step of extrusion-molding a kneaded product of a metal compound by using the multi-hole extrusion die according to the present invention to produce  
20 metal compound extrusion-molded bodies. Examples of the metal compound include metal compound catalysts, and the metal compound can contain, for example, molybdenum, bismuth, phosphorus, vanadium, iron, cobalt, chromium, aluminum, strontium, germanium, boron, arsenic, selenium, silver, silicon, sodium, tellurium, lithium, antimony, potassium, barium, magnesium, titanium, manganese, copper, zinc, zirconium, niobium, tungsten, tantalum, calcium, tin, gallium,  
25 cerium, lanthanum, rubidium, cesium, or thallium. In the case that the metal compound is a metal compound catalyst, catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance, can be produced through extrusion molding of a kneaded product of the metal compound by using the multi-hole extrusion die according to  
30 the present invention. It is preferable for the metal compound catalyst to contain molybdenum, from the viewpoint of achievement of high catalyst performance.

[0043]

[Method for producing catalyst extrusion-molded bodies for production of unsaturated aldehyde and/or unsaturated carboxylic acid]

The multi-hole extrusion die according to the present invention can be suitably used for a method for producing catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid. For example, the multi-hole extrusion die according to the present invention can be suitably used for the following methods set forth in (i)

5 to (iii):

(i) a method for producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid, the method including a step of extrusion-molding a kneaded product of a catalyst for production of acrolein and acrylic acid by using the multi-hole extrusion die according to the present invention, wherein the catalyst extrusion-molded bodies for production of acrolein and acrylic acid are for use in production of acrolein and acrylic acid through gas-phase catalytic oxidation of propylene with molecular oxygen, and at least contain molybdenum and bismuth;

10 (ii) a method for producing catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid, the method including a step of extrusion-molding a kneaded product of a catalyst for production of methacrolein and methacrylic acid by using the multi-hole extrusion die according to the present invention, wherein the catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid are for use in production of methacrolein and methacrylic acid through gas-phase catalytic oxidation of isobutylene and/or tertiary butyl alcohol with molecular oxygen, and at least contain molybdenum and bismuth; and

15 (iii) a method for producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid, the method including a step of extrusion-molding a kneaded product of a catalyst for production of an unsaturated carboxylic acid by using the multi-hole extrusion die according to the present invention, wherein the catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid are for use in production of an unsaturated carboxylic acid through gas-phase catalytic oxidation of an unsaturated aldehyde with molecular oxygen, and  
25 contain molybdenum and contains phosphorous and/or vanadium.

[0044]

The methods set forth in (i) to (iii) enable production of catalyst extrusion-molded bodies for production of an unsaturated aldehyde and/or unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance. In the method set forth in (iii), it is preferable that the unsaturated aldehyde be (meth)acrolein and the unsaturated carboxylic acid be (meth)acrylic acid, from the viewpoint that catalyst extrusion-molded bodies for production of (meth)acrolein and/or (meth)acrylic acid, the catalyst extrusion-molded bodies more consistently having high quality and high catalytic performance, can be produced. Hereinafter, the method set forth in (iii) for producing catalyst

extrusion-molded bodies for production of an unsaturated carboxylic acid will be specifically described as an example. However, the other methods can be similarly implemented.

[0045]

<Method for producing catalyst extrusion-molded bodies for production of unsaturated carboxylic acid>

The method set forth in (iii) is a method for producing catalyst extrusion-molded bodies containing molybdenum and containing phosphorous and/or vanadium as a catalyst component for production of an unsaturated carboxylic acid, where the catalyst extrusion-molded bodies are for use when an unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid corresponding to the unsaturated aldehyde, and the method can include the following step (1) to step (4): (1) a step of producing particles containing the catalyst component; (2) a step of kneading a composition containing the particles to obtain a kneaded product; (3) a step of extrusion-molding the kneaded product to obtain catalyst extrusion-molded bodies; and (4) a step of drying the catalyst extrusion-molded bodies. In the step (3), the kneaded product is extrusion-molded by using the multi-hole extrusion die according to the present invention. Through production of catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid by using this method, catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid, the catalyst extrusion-molded bodies consistently having high quality and high catalytic performance, can be obtained.

[0046]

(Step (1))

In the step (1), particles containing catalyst components are produced. The catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid at least contain molybdenum and contain phosphorus and/or vanadium as catalyst components. In addition to molybdenum, phosphorus, and/or vanadium, the catalyst extrusion-molded bodies can contain, for example, iron, cobalt, chromium, aluminum, strontium, germanium, boron, arsenic, selenium, silver, silicon, sodium, tellurium, lithium, antimony, potassium, barium, magnesium, titanium, manganese, copper, zinc, zirconium, niobium, tungsten, tantalum, calcium, tin, bismuth, gallium, cerium, lanthanum, rubidium, cesium, or thallium as a catalyst component. The catalyst extrusion-molded bodies may contain one of them, or contain two or more of them.

[0047]

The method for producing particles containing the catalyst components is not limited, and examples thereof include a method in which an aqueous slurry containing the catalyst

components is dried and further ground, as necessary, into the form of particulates. Examples of the raw material for the catalyst components contained in the aqueous slurry include oxides, sulfates, nitrates, carbonates, hydroxides, ammonium salts, and halides of the elements which are described above as catalyst components. Examples of the molybdenum raw material include ammonium paramolybdate and molybdenum trioxide. Examples of the vanadium raw material include ammonium metavanadate. One raw material or two or more raw materials may be used for each element of these catalyst components. The method for preparing an aqueous slurry containing the catalyst components is not limited, and various methods which do not cause uneven distribution of components, such as a precipitation method and an oxide-mixing method, can be used.

[0048]

The method for drying the aqueous slurry containing the catalyst components into particulate matters is not limited, and, for example, a method of drying with a spray dryer, a method of drying with a slurry dryer, a method of drying with a drum dryer, or a method of grinding a lump of a dried product obtained through evaporation drying is applied. Among them, the method of drying with a spray dryer is preferred because particles are obtained at the completion of drying and the shape of the obtained particles is a uniform sphere. In the case of drying with a spray dryer, the inlet temperature of the spray dryer is preferably 100 to 500°C. The outlet temperature of the spray dryer is preferably 100°C or higher, and more preferably 105 to 200°C. Dried particles obtained may be heat-treated (calcined) at 200 to 500°C, as necessary. The conditions for the heat treatment are not limited, and the heat treatment can be performed under oxygen flow, air flow, or nitrogen flow. The duration for the heat treatment is appropriately set in accordance with a catalyst intended.

[0049]

(Step (2))

In the step (2), a composition containing the particles obtained in the step (1) is kneaded to obtain a kneaded product. It is preferable to knead a composition as a mixture of the particles obtained in the step (1) and a liquid to obtain a kneaded product, from the viewpoint of effective pore formation for a catalyst. The liquid is preferably water or an alcohol. Examples of the alcohol include lower alcohols such as ethanol, methyl alcohol, propyl alcohol, and butyl alcohol. One liquid may be used, or two or more liquids may be used in combination. However, it is preferable that at least an alcohol be contained. The amount of the liquid to be used is appropriately determined in accordance with, for example, the type and size of the particles and the type of the liquid.

[0050]

It is preferable to add a molding aid such as an organic binder in addition to the particles and the liquid, from the viewpoint that enhanced strength is imparted to a catalyst. Examples of the molding aid include methyl cellulose, ethyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose, hydroxybutylmethyl cellulose, ethylhydroxyethyl cellulose, and hydroxypropyl cellulose. One of them may be used, or two or more of them may be used in combination. In addition to them, for example, an inorganic compound such as diatomaceous earth, graphite, an inorganic fiber such as a glass fiber and a ceramic fiber, or a carbon fiber may be added to the composition.

[0051]

The apparatus to knead the composition is not limited, and, for example, a batch kneader provided with a double-arm impeller, or a continuous kneader of, for example, rotating and reciprocating shaft type or self-cleaning type can be used. However, a batch kneader is preferred because the condition of a kneaded product can be checked during kneading.

[0052]

(Step (3))

In the step (3), the kneaded product obtained in the step (2) is extrusion-molded to obtain catalyst extrusion-molded bodies. Any method at least including a step of extrusion-molding the kneaded product by using the multi-hole extrusion die according to the present invention is available for extrusion molding of the kneaded product, without limitation. For example, the kneaded product may be directly molded into a final shape by using a screw extruder or a piston extruder. Alternatively, the kneaded product may be primary-molded to obtain a primary molded article and the primary molded article may then be secondary-molded into a final shape by using a piston molding machine. Among them, the method of primary molding followed by secondary molding is preferred. By performing molding in two steps, bending or the like of an article of a final shape is less likely to occur on extrusion, resulting in an enhanced yield of a product. In addition, molding can be performed with uniform force, and unnecessary inclusion of air is less likely to occur. As a result, homogeneous catalyst extrusion-molded bodies can be obtained, which provides a lower powdering rate in filling a reaction tube with the catalyst extrusion-molded bodies and enhanced selectivity for unsaturated carboxylic acids. Since smoother extrusion molding can be achieved than in the method of extrusion-molding the kneaded product directly into a final shape by using a screw extruder or the like, it is possible to perform soft molding in which an unnecessary load is not imposed to

catalyst particles during molding, and in which the catalyst particles do not collapse. Therefore, preferable pores are generated in a catalyst obtained. Thus, a catalyst superior in catalytic activity and selectivity for unsaturated carboxylic acids can be obtained.

[0053]

5           Now, the method of primary molding followed by secondary molding will be described. Although the primary molding process through the step (2) and the step (3) can be performed in a continuous manner by using a single screw extruder or a plurality of screw extruders, it is preferable to knead by using a batch kneader and to perform primary molding by using a screw extruder or a piston extruder, from the viewpoint that the condition of kneading can be checked  
10 during kneading and from the viewpoint of high productivity. The shape into which the kneaded product is primary-molded is not limited. In the case that a piston molding machine is used in secondary molding, the shape of a primary molded article is preferably a circular column having a diameter 0.5 times or more and less than 1 time as large as the cylinder diameter of a piston molding machine for secondary molding, and more preferably a circular column having a  
15 diameter 0.8 times or more and less than 1 time as large as the cylinder diameter of a piston molding machine for secondary molding. By virtue of the diameter 0.5 times or more as large as the cylinder diameter of a piston molding machine for secondary molding, unnecessary inclusion of air is less likely to occur in secondary molding, and the number of times of primary molding can be reduced and as a result the catalyst particles undergo a lower load. By virtue of  
20 the diameter less than 1 time as large as the cylinder diameter of a piston molding machine for secondary molding, it is easy to fill a piston molding machine with a primary molded article.

[0054]

The strength of a catalyst is higher as the specific gravity of a primary molded article is higher, and the selectivity of a catalyst for unsaturated carboxylic acids is enhanced as the  
25 specific gravity of a primary molded article is lower. Accordingly, the specific gravity of a primary molded article is preferably 1.5 to 3.5 kg/L, more preferably 2.0 to 2.9 kg/L, and even more preferably 2.2 to 2.7 kg/L, in view of the strength of a catalyst and the selectivity of a catalyst for unsaturated carboxylic acids. Specific gravity is a value calculated by dividing the mass of a primary molded article by the volume of the primary molded article, where the mass  
30 includes that of moisture.

[0055]

When the primary molded article obtained through primary molding is subsequently secondary-molded into a final shape, a piston molding machine, a screw molding machine, etc., can be used. However, use of a piston molding machine is preferred. It is preferable to use

the multi-hole extrusion die according to the present invention in secondary molding, and it is more preferable to use the multi-hole extrusion die according to the present invention in secondary molding with a piston molding machine. In the case that the multi-hole extrusion die according to the present invention is used, the above-described conditions can be used as the conditions for extrusion molding. There is a tendency that drying of the kneaded product or primary molded article proceeds particularly in the case that the kneaded product at least contains an alcohol as the liquid. However, by using the breaker plate according to the present invention, it is possible to pulverize and re-disperse the primary molded article which has been partially dried and whose flowability has been lowered. In addition, differential pressures at the die holes can be uniform through the effect of the breaker plate, resulting in homogenization of the quality of a catalyst such as the shape, specific gravity, and pore distribution to lead to enhanced catalyst performance.

[0056]

The shape of a secondary molded article is not limited, and can be appropriately determined in view of easiness in filling a reaction tube, porosity, unevenness of filling, pressure loss, reactivity, selectivity for an intended component and the like when the reaction is performed. For example, a primary molded article can be molded into any shape such as a ring, a circular column, and a pentagram. When a primary molded article is molded with a piston molding machine, it is preferable not to perform vacuum deaeration so as not to reduce the pore volume of a catalyst.

[0057]

#### (Step (4))

In the step (4), the catalyst extrusion-molded bodies obtained in the step (3) is dried. The drying method is not limited, and hot-air drying, far-infrared drying, microwave drying or another drying method is arbitrarily used. The drying conditions are appropriately determined in accordance with an intended liquid content. The catalyst extrusion-molded bodies dried can be calcined, as necessary. In the case that the particles have been calcined in the step (1) and an organic binder or the like is not used, however, calcination can be omitted. In the case that an organic binder or the like is used, on the other hand, it is preferable to perform calcination not in the step (1) but in the step (4) because of simplicity of processing. The calcination conditions are not limited, and, for example, calcination is performed in an atmosphere of air or nitrogen gas in a temperature range of 200 to 600°C. Thereby, catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid can be obtained.

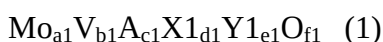
[0058]

The catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid produced by using the method according to the present invention can be used, for example, for production of acrylic acid through oxidation of acrolein and production of methacrylic acid through oxidation of methacrolein.

5 [0059]

In the case that the catalyst for production of an unsaturated carboxylic acid produced by using the method according to the present invention is used for production of acrylic acid through oxidation of acrolein, it is preferable for the catalyst to have a composition represented by the following formula (1).

10 [0060]

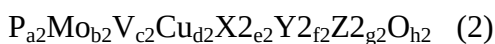


In the formula (1), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively; A represents at least one element selected from the group consisting of iron, cobalt, chromium, aluminum, and strontium; X1 represents at least one element selected from the group consisting of germanium, boron, arsenic, selenium, silver, silicon, sodium, tellurium, lithium, antimony, phosphorus, potassium, and barium; Y1 represents at least one element selected from the group consisting of magnesium, titanium, manganese, copper, zinc, zirconium, niobium, tungsten, tantalum, calcium, tin, and bismuth; a1, b1, c1, d1, and e1 represent the atomic ratios of the corresponding elements, and in the case of a1 = 12, then b1 = 0.01 to 6, c1 = 0 to 5, d1 = 0 to 10, and e1 = 0 to 5 are satisfied; and f1 represents the number of oxygen atoms necessary for satisfying the valences of the components.

[0061]

In the case that the catalyst for production of an unsaturated carboxylic acid produced by using the method according to the present invention is used for production of methacrylic acid through oxidation of methacrolein, it is preferable for the catalyst to have a composition represented by the following formula (2).

[0062]



In the formula (2), P, Mo, V, Cu, and O represent phosphorus, molybdenum, vanadium, copper, and oxygen, respectively; X2 represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, selenium, silicon, tungsten, boron, and silver; Y2 represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, manganese, cobalt, barium, gallium, cerium, and lanthanum; Z2 represents at least one element selected from the group consisting of potassium,

rubidium, cesium, and thallium; a<sub>2</sub>, b<sub>2</sub>, c<sub>2</sub>, d<sub>2</sub>, e<sub>2</sub>, f<sub>2</sub>, and g<sub>2</sub> represent the atomic ratios of the corresponding elements, and in the case of b<sub>2</sub> = 12, then a<sub>2</sub> = 0.5 to 3, c<sub>2</sub> = 0.01 to 3, d<sub>2</sub> = 0 to 2, e<sub>2</sub> = 0 to 3, f<sub>2</sub> = 0 to 3, and g<sub>2</sub> = 0.01 to 3 are satisfied; and h<sub>2</sub> represents the number of oxygen atoms necessary for satisfying the valences of the components. It should be noted that each of the catalyst compositions is calculated from the amounts of raw materials charged in production of the catalyst.

[0063]

[Method for producing unsaturated aldehyde and/or unsaturated carboxylic acid]

The method for producing acrolein and acrylic acid according to the present invention includes: a step of producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid by using the method set forth in (i); and a step of filling a reactor with the extrusion-molded bodies and subjecting propylene to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[0064]

The method for producing methacrolein and methacrylic acid according to the present invention includes: a step of producing catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid by using the method set forth in (ii); and a step of filling a reactor with the extrusion-molded bodies and subjecting isobutylene and/or tertiary butyl alcohol to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[0065]

The method for producing an unsaturated carboxylic acid according to the present invention includes: a step of producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid by using the method set forth in (iii); and a step of filling a reactor with the extrusion-molded bodies and subjecting an unsaturated aldehyde to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[0066]

These methods each enable production of the corresponding intended product with a high reaction rate and high selectivity. Hereinafter, the method for producing an unsaturated carboxylic acid will be specifically described as an example. However, the other methods can be similarly implemented.

[0067]

<Method for producing unsaturated carboxylic acid>

In the method for producing an unsaturated carboxylic acid according to the present invention, catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid are

produced by using the method according to the present invention, and a reactor is filled with the catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid and an unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen by using the catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid.

- 5 This method enables production of an unsaturated carboxylic acid from an unsaturated aldehyde with a high reaction rate and high selectivity.

[0068]

- 10 In the method according to the present invention, a reaction tube made of, for example, stainless steel is filled with the catalyst extrusion-molded bodies according to the present invention to form a catalyst layer. Then, a raw material gas containing an unsaturated aldehyde and molecular oxygen as reaction raw materials is allowed to flow through the catalyst layer for gas-phase catalytic oxidation of the unsaturated aldehyde, and thereby an unsaturated carboxylic acid corresponding to the unsaturated aldehyde can be produced. Examples of the unsaturated aldehyde include acrolein and methacrolein. One of them may be used, or two or more of them  
15 may be used in combination.

[0069]

- 20 Although the concentration of the unsaturated aldehyde in the raw material gas can be varied within a broad range, the concentration is preferably 1 to 20 vol%, and more preferably 3 to 10 vol%. The unsaturated aldehyde as a raw material may contain a small quantity of impurities including water and saturated lower aldehydes, and these impurities have substantially no effect on the reaction. Although use of air as the source of molecular oxygen is economical, air enriched with pure oxygen can be used, if necessary. The oxygen concentration of the raw material gas is preferably 0.3 to 4, and more preferably 0.4 to 2.5 as a mole ratio to the unsaturated aldehyde. It is preferable for the raw material gas to contain water in addition to  
25 the unsaturated aldehyde and molecular oxygen. It is preferable to dilute the raw material gas with an inert gas before use. The reaction pressure is preferably from atmospheric pressure to several hundred kPaG. The reaction temperature is preferably 200 to 430°C, and more preferably 220 to 400°C. The catalyst extrusion-molded bodies may be diluted with an inert carrier such as silica, alumina, silica-alumina, silicon carbide, titania, magnesia, ceramic balls,  
30 and stainless steel in the reaction tube.

## EXAMPLE

[0070]

Hereinafter, the present invention will be specifically described with reference to

Example and Comparative Examples. "Part" in Example and Comparative Examples is by mass. A batch kneader provided with a double-arm impeller was used for kneading. Analysis for raw material gas and reaction gas was performed by using gas chromatography. In Example and Comparative Examples, an unsaturated aldehyde was used as a raw material. Reaction rates of an unsaturated aldehyde (hereinafter, referred to as "reaction rate") and selectivities for an unsaturated carboxylic acid produced in Example and Comparative Examples were calculated by using the following equations.

[0071]

$$\text{Reaction rate (\%)} = A/B \times 100$$

$$\text{Selectivity for unsaturated carboxylic acid (\%)} = C/A \times 100$$

Here, A denotes the number of moles of an unsaturated aldehyde reacted; B denotes the number of moles of an unsaturated aldehyde fed; and C denotes the number of moles of an unsaturated carboxylic acid produced.

[0072]

The bulk specific gravity of particles containing a catalyst component was measured by using a method described in JIS K 6721. The specific gravity of a primary molded article was calculated by dividing the mass of a primary molded article by the volume of the primary molded article, where the mass included that of moisture. Particle crushing strength was measured by using a micro compression tester (trade name: MCTM-200, produced by Shimadzu Corporation). Mean particle crushing strength is the mean of measurements for 30 particles. The standard deviation of the lengths of catalyst extrusion-molded bodies was calculated from measurement results for 100 pieces of catalyst extrusion-molded bodies. The fraction of sieved-out products (hereinafter, referred to as "nonconformity") was calculated by using the following equation.

[0073]

$$\text{Nonconformity (\%)} = (B + C) / A$$

Here, A denotes the total mass of molded bodies after being dried; B denotes the mass of small-sized products sieved out with a metal mesh made of SUS304 and having a sieve opening of 3 mm × 6 mm and a wire diameter of 1.2 mm; and C denotes the mass of products of 7 mm or longer removed through individual measurements.

[0074]

(Example 1)

In 4000 parts of pure water, 1000 parts of molybdenum trioxide, 34 parts of ammonium metavanadate, 80 parts of 85% by mass aqueous solution of phosphoric acid, and 14 parts of

copper nitrate were dissolved, and the resultant was warmed to 95°C with stirring, and stirred for 3 hours with the solution temperature kept at 95°C. After cooling to 40°C, a solution obtained by dissolving 135 parts of cesium bicarbonate in 200 parts of pure water was added with stirring by using a rotor blade stirrer, and the resultant was stirred for 15 minutes. Subsequently, a solution obtained by dissolving 107 parts of ammonium carbonate in 200 parts of pure water was added, and the resultant was further stirred for 20 minutes. The resulting aqueous slurry containing catalyst components is dried with a spray dryer to afford dried spherical particles having a mean particle diameter of 38  $\mu\text{m}$  and containing catalyst components. Here, the mean particle crushing strength and bulk specific gravity of the dried spherical particles were  $3.9 \times 10^{-3}$  N and 0.87 kg/L, respectively.

[0075]

To 500 parts of the dried spherical particles, 25 parts of hydroxypropyl cellulose was added and dry-blended. Therein, 20 parts of pure water and 80 parts of ethanol were mixed, and the mixture was kneaded by using a kneader until the mixture was converted into a clay-like substance to afford a kneaded product.

[0076]

Thereafter, the kneaded product of an indefinite shape was extrusion-molded by using a piston molding machine to afford a primary molded article with the shape of a circular column having a diameter of 100 mm and a length of 350 mm. Here, the specific gravity of the primary molded article was 2.30 kg/L. Subsequently, the primary molded article was extrusion-molded by using a piston extrusion molding machine including a cylinder having a cylinder diameter of 120 mm (D1 in Figure 1) and a length of 400 mm and a multi-hole extrusion die including 20 die holes each having a diameter of 5.5 mm and disposed in a concentric circle pattern to afford catalyst extrusion-molded bodies with the shape of a circular column having an outer diameter of 5.5 mm and a length of 5 mm.

[0077]

As illustrated in Figure 1, the multi-hole extrusion die included a breaker plate 4 provided with a plurality of through-holes 7 each having a size, a, of 5 mm in a radial pattern and having a thickness, b, of 8 mm ( $b/a = 1.6$ ) with an aperture ratio of 36.5%, and a die body 1 including a flow adjuster 3 and die holes 6, the flow adjuster 3 having the shape of a truncated cone with an angle,  $\alpha$ , of 118° and having a structure in which a circular flat surface having a diameter, D3, of 20 mm was provided at the tip to support a center section of the breaker plate 4. No through-hole 7 was included in the portion of the breaker plate 4 in contact with the flat section of the flow adjuster 3 (the center section of the breaker plate 4). The diameter, D2, of

the portion including no through-hole 7 was 25 mm. The breaker plate 4 and the flat section of the flow adjuster 3 were only contacting with each other without being fixed with bolts or the like. The breaker plate 4 consisted of SUS630H900, which had a proof stress of 1175 MPa or higher, and the structural members other than the breaker plate 4 each consisted of SUS304. A cutting blade rotating around the center section of the die surface as a rotational axis was used to cut the catalyst extrusion-molded bodies. Vacuum deaeration was not performed in molding. The extrusion pressure was measured by using a nozzle provided on the wall surface of the cylinder 2 on the primary side of the breaker plate 4.

[0078]

The catalyst extrusion-molded bodies were dried at 130°C for 6 hours, and the standard deviation of the lengths of the catalyst extrusion-molded bodies and the fraction of sieved-out products were determined, and the catalyst extrusion-molded bodies were then heat-treated under air flow at 380°C for 5 hours to afford catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid. The elemental composition of the catalyst extrusion-molded bodies obtained was  $P_{1.2}Mo_{12}V_{0.5}Cu_{0.1}Cs_{1.2}$  with oxygen excluded.

[0079]

A reaction tube made of stainless steel was filled with the catalyst extrusion-molded bodies, and a raw material gas consisting of 5 vol% of methacrolein, 10 vol% of oxygen, 10 vol% of water vapor, and 75 vol% of nitrogen was allowed to pass through the catalyst layer for a contact time of 4.3 seconds, and reacted at 300°C. The results are shown in Table 1.

[0080]

(Comparative Example 1)

Catalyst extrusion-molded bodies were produced and reaction was performed in the same manner as in Example 1 except that, as illustrated in Figure 2, the breaker plate 4 was not provided to the multi-hole extrusion die and the shape of the flow adjuster 3 was changed, from the shape of a truncated cone with a flat surface at the tip, to the shape of a cone with an apex at the tip. The results are shown in Table 1.

[0081]

(Comparative Example 2)

As illustrated in Figure 3, the shape of the flow adjuster 3 in the multi-hole extrusion die was changed, from the shape of a truncated cone with a flat surface at the tip, to the shape of a cone with an apex at the tip. The thickness of the breaker plate 4, b, was changed to 2 mm, and additionally the portion of the breaker plate 4 in contact with the tip of the flow adjuster 3 (the center section of the breaker plate 4) was changed so that the portion included through-holes 7.

Catalyst extrusion-molded bodies were produced in the same manner as in Example 1 except these points. However, an abnormal sound was generated after initiation of extrusion molding, and thus the operation was immediately stopped. The inside of the apparatus was checked to find that the entire of the breaker plate 4, in particular, the center section of the breaker plate 4 was deformed and broken.

[0082]

(Comparative Example 3)

Catalyst extrusion-molded bodies were produced in the same manner as in Example 1 except that the thickness of the breaker plate 4, b, was changed to 30 mm. However, the extrusion pressure reached 35 MPaG, which was the upper limit for the apparatus, after initiation of extrusion molding, and thus the operation was immediately stopped.

[0083]

(Comparative Example 4)

Catalyst extrusion-molded bodies were produced and reaction was performed in the same manner as in Example 1 except that the diameter, a, of through-holes 7 of the breaker plate 4 was changed to 1.5 mm. The results are shown in Table 1. However, the extrusion pressure exceeded 30 MPaG after initiation of extrusion molding, and the extrusion pressure reached 35 MPaG, which was the upper limit of the apparatus, in the final stage of molding, and thus the operation was stopped. Thereafter, the inside of the apparatus was opened, and the condition of the breaker plate 4 was checked to find that almost all the through-holes 7 were clogged.

[0084]

(Comparative Example 5)

As illustrated in Figure 3, the shape of the flow adjuster 3 in the multi-hole extrusion die was changed, from the shape of a truncated cone with a flat surface at the tip, to the shape of a cone with an apex at the tip. The material of the breaker plate 4 was changed to SS400 (proof stress: lower than 300 MPa), and additionally the portion of the breaker plate 4 in contact with the tip of the flow adjuster 3 (the center section of the breaker plate 4) was changed so that the portion included through-holes 7. Catalyst extrusion-molded bodies were produced in the same manner as in Example 1 except these points. The results are shown in Table 1. However, the catalyst extrusion-molded bodies obtained in the first extrusion molding were blackened because the surface of the breaker plate 4 had not been subjected to electroless nickel plating or the like, and thus the operation was immediately stopped. Thereafter, the inside of the apparatus was opened, and the condition of the breaker plate 4 was checked to find corrosion for the whole surface and find that the entire of the breaker plate 4, in particular, the center portion of the

breaker plate 4 was deformed.

[0085]

(Comparative Example 6)

As illustrated in Figure 3, the shape of the flow adjuster 3 in the multi-hole extrusion die was changed, from the shape of a truncated cone with a flat surface at the tip, to the shape of a cone with an apex at the tip. The material of the breaker plate 4 was changed to SUS304 (proof stress: lower than 300 MPa), and additionally the portion of the breaker plate 4 in contact with the tip of the flow adjuster 3 (the center section of the breaker plate 4) was changed so that the portion included through-holes 7. Catalyst extrusion-molded bodies were produced and reaction was performed in the same manner as in Example 1 except these points. The results are shown in Table 1. After the completion of production of the catalyst extrusion-molded bodies, the inside of the apparatus was opened, and the condition of the breaker plate 4 was checked to find that the entire of the breaker plate 4, in particular, the center portion of the breaker plate 4 was deformed.

[0086]

In Example 1, in which the multi-hole extrusion die according to the present invention was used, the obtained catalyst had a small standard deviation of the lengths of the catalyst extrusion-molded bodies and a small value of nonconformity, and exhibited a high reaction rate and high selectivity for methacrylic acid.

[0087]

In Comparative Example 1, in which the breaker plate was not provided, in contrast, the differential pressures at the die holes were not uniform, and not only a larger standard deviation of the lengths of the catalyst extrusion-molded bodies and a larger value of nonconformity were provided, but also a lower reaction rate and lower selectivity for methacrylic acid were provided.

[0088]

In Comparative Example 2, in which the thickness of the breaker plate,  $b$ , was changed to 2 mm, the value of  $b/a$  was lower than 0.5, and it is inferred that the breaker plate had low strength and as a result failed to endure the extrusion pressure.

[0089]

In Comparative Example 3, in which the thickness of the breaker plate,  $b$ , was changed to 30 mm, the value of  $b/a$  was 3.0 or more, and it is inferred that higher pressure loss was generated.

[0090]

In Comparative Example 4, in which the diameter,  $a$ , of through-holes of the breaker

plate was changed to 1.5 mm, the value of b/a was 3.0 or more, and it is inferred that larger differential pressure was generated in the breaker plate to cause clogging. It is further inferred that strong shear was generated in the primary molded body to lower the catalyst performance, which resulted in a lower reaction rate and lower selectivity for methacrylic acid.

5 [0091]

For Comparative Example 5, in which the material of the breaker plate was changed to SS400, it is inferred that the catalyst extrusion-molded bodies were reduced.

[0092]

10 For Comparative Example 6, in which the material of the breaker plate was changed to SUS304, and additionally modification was made so that the center section of the breaker plate included through-holes, it is inferred that the strength of the breaker plate was lower. In addition, the modification such that the flow adjuster had the shape of a cone having an apex, instead of the shape of a truncated cone having a flat surface at the tip, is inferred to disable stable supporting of the breaker plate.

15 [0093]

[Table 1]

|                                                                   |                              |      | Example 1    | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 | Comparative Example 5 | Comparative Example 6 |
|-------------------------------------------------------------------|------------------------------|------|--------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Shape of tip of flow adjuster                                     |                              |      | flat surface | with apex             | with apex             | flat surface          | flat surface          | flat surface          | with apex             |
| Breaker plate                                                     | Proof stress of material     | MPa  | ≥1175        | -                     | ≥1175                 | ≥1175                 | ≥1175                 | <300                  | <300                  |
|                                                                   | Diameter of through-hole (a) | mm   | 5            | -                     | 5                     | 5                     | 1.5                   | 5                     | 5                     |
|                                                                   | Thickness (b)                | mm   | 8            | -                     | 2                     | 30                    | 8                     | 8                     | 8                     |
|                                                                   | b/a                          | -    | 1.6          | -                     | 0.4                   | 6                     | 5.3                   | 1.6                   | 1.6                   |
| Extrusion pressure                                                |                              | MPaG | 9.7          | 7.9                   | -                     | -                     | >30                   | 12.1                  | 11.2                  |
| Standard deviation of lengths of catalyst extrusion-molded bodies |                              | mm   | 0.46         | 1.23                  | -                     | -                     | 0.42                  | -                     | 0.51                  |
| Nonconformity                                                     |                              | %    | 1.0          | 5.3                   | -                     | -                     | 2.0                   | -                     | 2.4                   |
| Reaction rate                                                     |                              | %    | 53.5         | 51.8                  | -                     | -                     | 50.2                  | -                     | 50.8                  |
| Selectivity for methacrylic acid                                  |                              | %    | 94.0         | 92.7                  | -                     | -                     | 91.5                  | -                     | 91.8                  |

[0094]

20 The present application claims priority to Japanese Patent Application No. 2016-33044 filed on February 24, 2016, and the disclosure is totally incorporated herein.

[0095]

Although the present invention has been described with reference to the embodiments and Example, the present invention is not limited to the embodiments and Example. Various modifications which those skilled in the art can appreciate can be made for the configuration and detail of the present invention within the scope of the present invention.

5

#### Reference Signs List

[0096]

- |      |               |
|------|---------------|
| 1    | die body      |
| 2    | cylinder      |
| 10 3 | flow adjuster |
| 4    | breaker plate |
| 5    | piston head   |
| 6    | die hole      |
| 7    | through-hole  |

15

## CLAIMS

### [Claim 1]

A multi-hole extrusion die comprising:

5 a die body including die holes and a flow adjuster that allows a material to be molded to evenly flow into the die holes; and

a breaker plate comprising a material having a proof stress of 300 MPa or higher, the breaker plate being provided with a plurality of through-holes each having a size of a (mm), and the breaker plate having a thickness of b (mm), wherein

10 b/a is 0.5 or more and less than 3.0, and

the multi-hole extrusion die has a structure in which a center section of the breaker plate is supported on a flat section provided to the flow adjuster of the die body.

### [Claim 2]

15 A method for producing metal compound extrusion-molded bodies, comprising a step of extrusion-molding a kneaded product of a metal compound by using the multi-hole extrusion die according to claim 1 to produce metal compound extrusion-molded bodies.

### [Claim 3]

The method for producing metal compound extrusion-molded bodies according to claim 2, wherein the metal compound is a metal compound catalyst.

20 [Claim 4]

The method for producing metal compound extrusion-molded bodies according to claim 3, wherein the metal compound catalyst comprises molybdenum.

### [Claim 5]

25 The method for producing metal compound extrusion-molded bodies according to any one of claims 2 to 4, wherein the multi-hole extrusion die comprises a material that does not reduce the kneaded product.

### [Claim 6]

30 The method for producing metal compound extrusion-molded bodies according to any one of claims 2 to 5, wherein the breaker plate comprises at least one stainless steel material selected from the group consisting of martensitic stainless steel material, duplex stainless steel material, and precipitation-hardening stainless steel material.

### [Claim 7]

The method for producing metal compound extrusion-molded bodies according to any one of claims 2 to 6, wherein a member other than the breaker plate in the multi-hole extrusion

die comprises at least one stainless steel material selected from the group consisting of austenitic stainless steel material, martensitic stainless steel material, ferritic stainless steel material, duplex stainless steel material, precipitation-hardening stainless steel material, and superalloy.

[Claim 8]

5           The method for producing metal compound extrusion-molded bodies according to any one of claims 2 to 7, wherein extrusion pressure applied to the kneaded product in the extrusion-molding of the kneaded product by using the multi-hole extrusion die is 0.1 to 30 MPaG.

[Claim 9]

10           A method for producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid, comprising a step of extrusion-molding a kneaded product of a catalyst for production of acrolein and acrylic acid by using the multi-hole extrusion die according to claim 1, wherein

            the catalyst extrusion-molded bodies for production of acrolein and acrylic acid are for  
15   use in production of acrolein and acrylic acid through gas-phase catalytic oxidation of propylene with molecular oxygen, and at least comprise molybdenum and bismuth.

[Claim 10]

            A method for producing catalyst extrusion-molded bodies for production of  
methacrolein and methacrylic acid, comprising a step of extrusion-molding a kneaded product of  
20   a catalyst for production of methacrolein and methacrylic acid by using the multi-hole extrusion die according to claim 1, wherein

            the catalyst extrusion-molded bodies for production of methacrolein and methacrylic  
acid are for use in production of methacrolein and methacrylic acid through gas-phase catalytic  
oxidation of isobutylene and/or tertiary butyl alcohol with molecular oxygen, and at least  
25   comprise molybdenum and bismuth.

[Claim 11]

            A method for producing catalyst extrusion-molded bodies for production of an  
unsaturated carboxylic acid, comprising a step of extrusion-molding a kneaded product of a  
catalyst for production of an unsaturated carboxylic acid by using the multi-hole extrusion die  
30   according to claim 1, wherein

            the catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid  
are for use in production of the unsaturated carboxylic acid through gas-phase catalytic oxidation  
of an unsaturated aldehyde with molecular oxygen, and comprise molybdenum and comprise  
phosphorous and/or vanadium.

[Claim 12]

The method for producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid according to claim 11, wherein the unsaturated aldehyde is (meth)acrolein, and the unsaturated carboxylic acid is (meth)acrylic acid.

5 [Claim 13]

A method for producing acrolein and acrylic acid, comprising:

a step of producing catalyst extrusion-molded bodies for production of acrolein and acrylic acid by using the method according to claim 9; and

10 a step of filling a reactor with the extrusion-molded bodies and subjecting propylene to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[Claim 14]

A method for producing methacrolein and methacrylic acid, comprising:

a step of producing catalyst extrusion-molded bodies for production of methacrolein and methacrylic acid by using the method according to claim 10; and

15 a step of filling a reactor with the extrusion-molded bodies and subjecting isobutylene and/or tertiary butyl alcohol to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

[Claim 15]

A method for producing an unsaturated carboxylic acid, comprising:

20 a step of producing catalyst extrusion-molded bodies for production of an unsaturated carboxylic acid by using the method according to claim 11 or 12; and

a step of filling a reactor with the extrusion-molded bodies and subjecting the unsaturated aldehyde to gas-phase catalytic oxidation with molecular oxygen by using the extrusion-molded bodies.

25