reaction mechanism.

[0009] Many catalysts have already been reported for producing acrolein by the glycerin dehydration reaction.

[0010] Patent Document 1 (US 5,387,720) discloses a process for producing acrolein by glycerin dehydration on a variety of solid acids in gas phase and liquid phase. Hammett index is defined as +2 or less, more preferably -3 or less, so that corresponding catalyst is for example natural or synthetic silicon compounds such as mordenite, montmorillonite, zeolite, monobasic acids, dibasic acid, tribasic acids supported on alumina and titania; γ-alumina, ZnO/Al_2O_3, or heteropolyacids. It is believed that a problem shown in FR 695,931 of by-products which are generated in case of an iron phosphate catalyst system can be solved.

[0011] Patent Document 2 (WO2006/087084) teaches that a strong solid acid having Hammett index from -9 to -18 permits to produce acrolein at high activity by glycerin dehydration and to suppress degradation of catalyst.

[0012] Patent Document 3 (WO2009/044081) discloses a glycerin dehydration reaction effected in the presence of a catalyst containing oxygen, iron, phosphorus, and alkali metal, and one or more elements selected from alkali-earth metals (Al, Si, B, Co, Cr, Ni, V, Zn, Zr, Sn, Sb, Ag, Cu, Nb, Mo, Y, Mn, Pt, and Rh) and rare earths (La, Ce, and Sm).

[0013] Patent Document 4 (WO2009/128555) discloses a process for preparing acrolein comprising a glycerin dehydration reaction effected in the presence of a catalyst consisting of a compound in which protons in heteropolyacid are exchanged with more than one cation of elements selected from a group consisting of Group 1 to Group 16 of the periodic table.

[0014] Patent Document 5 (WO2010/046227) discloses a glycerin dehydration reaction effected in the presence of a catalyst containing

oxygen, phosphorus, and at least one element selected from a group consisting of vanadium, boron, and aluminum.

[0015] The conventional catalysts proposed in these prior documents, however, have certain problems such as a deposition of cokes which degrade the catalyst, and a development of secondary reactions such as an addition reaction of acrolein to hydroxy acetone, propionaldehyde, acetaldehyde, acetone, or glycerin, a polycondensation of glycerin, a formation of by-products such as cyclic glycerin ether, phenol, and poly aromatic compounds.

[0016] Therefore, to reduce generation of coke and degradation of catalysis and to suppress formation of by-products, such much detailed technology that physical properties of catalyst are limited as well as desirable catalytic active species are limited has been proposed.

[0017] Patent Document 6 (WO2007/058221) and Patent Document 7 (JP-A-2008-088149) disclose that an element of the Group 6 (tungsten, chromium, or molybdenum) or heteropolyacid is impregnated on an inorganic carrier containing at least one element selected from silicon, aluminum, titanium, and zirconium. The documents disclose in their claims that the inorganic carrier has a bimodal porous structure. The yield is improved when heteropolyacid is supported on a bipore silicon oxide carrier and the yield of higher than 80% is obtained comparing to a monopore silicon oxide carrier. However, the concentration of aqueous solution of glycerol is not high, and the proportion of hydroxy acetone which may be formed by dehydration of glycerin terminal is high. The prior documents disclose in their preferred examples that a carrier supporting heteropolyacid had the specific surface area of 30 to 1500 m^2/g, bimodal pore structure, macro pore of 0.5 to 200 μm, nanopore of 1 to 50 nm, as well as a pore volume of 0.3 to 4 cm^3/g.

[0018] Patent Document 8 (JP-A-2010-253374) discloses that a bipore silicon oxide carrier supporting boron phosphate thereon can prevent a decrease of the yield of acrolein in time in comparison to a monopore silicon oxide carrier. The active species to be supported are at least

one element selected from Al, Zr, and B, and/or crystalline salt of at least one element selected from rare earth elements and phosphorus. Its physical properties are characterized in that the carrier contains 90 mass % of silica, macropore of 0.1 to 30 μm, nanopore of 1 to 50 nm, and the carrier is amorphous. There is no detailed limitation of a pore volume of bipore and a relation between a volumetric basis mode diameter and catalytic behavior of the bipore carrier.

[0019] Patent Document 9 (JP-A-2007-301506) reports that the conversion of glycerin and the yield of acrolein in catalytic glycerin dehydration can be improved by using a molded catalyst of crystalline metallosilicate having a ratio of Si/T (T = Al, B, Ti, Cu, In, Cr, Fe, Co, Ni, Zn, or Ga) of less than 3000, a volumetric basis mode diameter of the molded catalyst measured by the mercury press-in method being smaller than 0.8 μm. This document describes primary and secondary pores of the metallosilicate, but is silent on a pore volume and volume ratio of bipores.

[0020] As explained above, the prior documents merely disclose some catalytic active species having limited physical parameters, such as a catalyst supporting the Group 6 element; a catalyst supporting heteropolyacid; a catalyst supporting crystalline salt of Al, Zr, B, and phosphorus; and metallosilicate. The prior documents also disclose some physical property parameters such as the specific surface area, a range of bipore diameters, and a cumulative pore volume of bipores. However the prior documents are silent on each pore volume of bipores and any pore volume ratios between mesopore and macropore.

[Citation List]
[Patent Literature]
[0021]

[Patent Document 1] US 5,387,720
[Patent Document 2] WO2006/087084
[Patent Document 3] WO2009/044081
[Patent Document 4] WO2009/128555
[Patent Document 5] WO2010/046227

simplified, which is very beneficial for industrial plants.

[Description of Embodiments]

[0032] The present catalyst for glycerin dehydration comprising a porous carrier, wherein the porous carrier includes at least one metal oxide selected from the group consisting TiO_2, SiO_2, Al_2O_3, ZrO_2, and Nb_2O_5, wherein the carrier includes a bimodal porous structure in which the volume ratio between a pore volume of mesopores having a pore size of more than 2 nm to less than 50 nm to a pore volume of macropores having a pore size of 50 nm or more is equal to or more than 0.5, and wherein the porous carrier configures to support a W-containing metal oxide thereon, or a metal oxide containing at least one element selected from the group consisting of P, Si, Mo, and V, in addition to the W-containing metal oxide thereon.

[0033] Physical properties of pores, such as a pore diameter and a pore volume of the present porous carrier, are determined by the mercury press-in method (mercury intrusion method) at a mercury surface tension of 480 dyn/cm with a mercury contact angle of 140°± by a mercury porosimetry ("Pore Master 60-GT" manufacuterd by Quanta Chrome Co.). Values or positions (nm) of mesopores and macropores shown in the present description are values of the maximum pore diameter of each pore obtained in a correlation graph having axis of ordinates of -dV/d(log d) [cc/g] which expresses how much mercury penetrate in the mercury press-in method (expressed in cc for logarithm μm for 1g of sample) and axis of abscissas of the pore diameter.

[0034] Namely, the phrases of "a pore size of more than 2 nm to less than 50 nm" and " a pore size of 50 nm or more" regarding the mesopore and macropore of the present porous carrier should mean that the value of the pore diameter of each pore is located at the peak maximal value. The mesopore may preferably be in a range of more than 2 nm to less than 50nm, and more preferably in a range of 10 to 30 nm. The macropore may preferably be 50 nm or more, more preferably in a range of 50 to 300 nm.

several Examples. The present invention is however not limited to the following Examples but covers those that are within the spirit of the present invention. In the Examples and Comparative Examples, the unit of "%" means mole %.

[0061] <Example 1>

Catalyst of PW/TiO_2 for dehydration reaction of glycerin was prepared as following. 13.2 g of phosphotungstic acid (Nippon Inorganic Color & Chemical Co., Ltd.) was dissolved in 100 ml of pure water. Separately, 100g of anatase TiO_2 pellets ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ~~×~~ x length of 5 mm; 48.2 m^2/g; 0.36 cc/g; pore volume ratio = 1.4) was placed on a porcelain dish onto which the above aqueous solution of phosphotungstic acid was added and left for 2 hours. The mixture was dried up at 120°C for 10 hours, and then calcinated in an air atmosphere at 500 °C for 3 hours.

[0062] The resulted catalyst was subjected to an evaluation test in a pass-through type fix bed reactor operated at ambient pressure. 30 cc of the catalyst was packed in a SUS reaction tube (20 mm diameter). An aqueous solution of 50 wt % of glycerin was pre-heated in a vaporizer heated at 330 °C and the resulted gasified glycerin was pumped and fed directly to the catalyst together with air flow (flow rate: 23.4 g/hr). The reactor containing the catalyst was heated to 290 °C. The feed stream had following composition: (glycerin : oxygen : nitrogen : water) = (4.7 mol % : 2.8 mol % : 68.5 mol % : 24.0 mol %). The GHSV was 2,020 h^{-1}. The resulted products were collected in a condenser as condensates, and the quantitative determination of all components was carried out by a gas chromatograph ("7890A" manufactured by Agilent; DB-WAX column). Factor of each product was corrected by the gas chromatograph to obtain absolute contents of the fed glycerin, remained glycerin, and products. The conversion of raw material (glycerin conversion), the selectivity of objective substance (acrolein selectivity), and the yield of objective substance (acrolein yield) were calculated by following equations:

[0063]

The conversion of raw material (%) = {(a mole number of material reacted) / (a mole number of material fed)} x 100

The selectivity of objective substance (%) = {(a mole number of objective substance obtained) / (a mole number of material reacted)} x 100

The yield of objective substance (%) = {(a mole number of objective substance obtained) / (a mole number of material fed)} x 100

The quantitative analysis was carried out in every several hours. The glycerin conversion and the acrolein yield were compared for each catalyst at a reaction time of 19 hours and 43 hours.

[0064] <Example 2>

The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm x length of 5 mm; 29.2 m^2/g; 0.30 cc/g; pore volume ratio = 1.5) was used as TiO_2. The result is shown in Table 1.

[0065] <Example 3>

The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm x length of 5 mm; 35.6 m^2/g; 0.33 cc/g; pore volume ratio = 1.1) was used as TiO_2. The result is shown in Table 1.

[0066] The cumulative pore volume, the ratio in pore volume, and the average pore diameter of Examples 2 and 3 are within a range of this invention. The results reveal that these catalysts show high glycerin conversion and high acrolein yield and reduced decrease of the glycerin conversion and of the acrolein yield, in spite of relatively lower specific surface area, comparing to Comparative Examples.

[0067] <Example 4>

The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ⊥–x length of 5 mm; 39.9 m^2/g; 0.36 cc/g; pore volume ratio = 1.3) was used as TiO_2. The result is shown in Table 1.

[0068] <Example 5>

The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ⊥–x length of 5 mm; 45.6 m^2/g; 0.36 cc/g; pore volume ratio = 1.4) was used as TiO_2. The result is shown in Table 1.

[0069] <Example 6>

Catalyst of W/TiO_2 for dehydration reaction of glycerin was prepared as following. 12.2 g of ammonium metatungustate (Nippon Inorganic Color & Chemical Co., Ltd.) was dissolved in 100 ml of pure water. Separately, 100g of anatase TiO_2 pellets ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ⊥–x length of 5 mm; 48.2 m^2/g; 0.36 cc/g; pore volume ratio = 1.4) was placed on a porcelain dish onto which the above aqueous solution of ammonium metatungustate was added and left for 2 hours. The mixture was dried up at 120°C for 10 hours, and then calcinated in an air atmosphere at 500 °C for 3 hours.

[0070] <Example 7>

The same operation as Example 1 was carried out, except that anatase TiO_2 ring ("ST 31119" manufactured by Saint-Gobain; diameter of 4.5 mm ⊥–x length of 5 mm; 54 m^2/g; 0.32 cc/g; pore volume ratio = 0.5) was used as TiO_2.

[0071] <Example 8>

The same operation as Example 1 was carried out, except that anatase TiO_2 trilobe ("ST 31119" manufactured by Saint-Gobain;

diameter of 4.5 mm ⊥–x length of 5 mm; 53 m^2/g; 0.40 cc/g; pore volume ratio = 0.9) was used as TiO_2.

[0072] <Example 9>

The same operation as Example 1 was carried out, except that anatase TiO_2 quadrilobe ("ST 31119" manufactured by Saint-Gobain; diameter of 4.5 mm ⊥–x length of 5 mm; 54 m^2/g; 0.38 cc/g; pore volume ratio = 0.9) was used as TiO_2. The same reaction estimation as Example 1 was carried out. The result is shown in Table 1.

[0073] <Comparative Example 1>

In the Comparative Examples, a sample of TiO_2 which is outside the scope of present invention was prepared and evaluated as following.

[0074] The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 sphere ("CS-300S" manufactured by Sakai Kagaku; diameter: 3.0 mm; 75 m^2/g; 0.40 cc/g; pore volume ratio = 0.4) was used as TiO_2. The result is shown in Table 1.

[0075] <Comparative Example 2>

The same experimental procedure and estimation as Example 1 were carried out, except that anatase TiO_2 sphere ("CS-300S" manufactured by Sakai Kagaku; diameter: 3.0 mm; 52 m^2/g; 0.32 cc/g; pore volume ratio = 0.3) was used as TiO_2. The result is shown in Table 1.

[0076] Catalysts of Comparative Examples 1 and 2 had the same or higher pore volume and specific surface area as Examples 1, 4, and 5, but the catalytic activity of Comparative Example 1 decreased much rapidly (comparison in the glycerin conversion and the acrolein yield at 19 hours and 43 hours). Comparative Example 1 has the ratio in pore volume of the macropores to the mesopores is 0.4 which is outside a requirement of higher than 0.5 of the present invention. The results reveal that the life of catalyst is influenced by the ratio of pore volumes.

[0077] <Comparative Example 3>

The same operation as Example 1 was carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ~~×~~ x length of 5 mm; 42.4 m^2/g; 0.26 cc/g; pore volume ratio = 1.6) was used as TiO_2. The same reaction estimation as Example 1 was carried out. The result is shown in Table 1.

[0078] The catalyst of Comparative Example 3 has similar specific surface area, average pore diameter, and pore volume as Examples 1 and 5, but the pore volume of 0.26 cc/g is outside the claimed range (0.30 cc/g or more). The result reveals that deteriorations in time of the glycerin conversion and of the acrolein yield are also influenced by the cumulative pore volume in addition to the specific surface, average pore diameter, and the ratio of pore volumes.

[0079] <Comparative Example 4>

~~In Example 6, t~~The same experimental procedure and estimation as Example ~~1~~ 6 was carried out, except that anatase TiO_2 pellet ("ST 31119" manufactured by Saint-Gobain; diameter of 3.2 mm ~~×~~ x length of 5 mm; 42.4 m^2/g; 0.26 cc/g; pore volume ratio = 1.6) was used as TiO_2. The same reaction estimation was carried out. The result is shown in Table 1.

[0080] By comparing Comparative Example 4 and Example 6, difference in physical properties of TiO_2 when the carrier supports a metal oxide consisting of tungsten oxide alone can be evaluated. A comparative carrier of Comparative Example 4 has same specific surface area, average pore diameter, and the ratio in pore volumes as Example 6, but the pore volume of 0.26 cc/g is outside the claimed range (0.30 cc/g or more), as similar to PW/TiO_2 of Comparative Example 3. The result reveals that deteriorations in time of the glycerin conversion and of the acrolein yield are also influenced by the ranges of physical properties in the case that a porous carrier supports a metal oxide consisting of tungsten oxide alone.

[0081]