

DESCRIPTION

Title of Invention

CATALYST FOR HYDROGENOLYSIS OF POLYHYDRIC ALCOHOL AND METHOD
FOR PRODUCING 1,3-PROPANEDIOL USING CATALYST FOR
HYDROGENOLYSIS OF POLYHYDRIC ALCOHOL

Technical Field

[0001]

The present invention relates to a catalyst for hydrogenolysis of a polyhydric alcohol (catalyst for polyhydric alcohol hydrogenolysis), where the catalyst enables selective and high-yield production of a corresponding hydrogenolysate from a polyhydric alcohol (e.g., glycerol). The present invention also relates to a method for producing 1,3-propanediol using the catalyst.

Background Art

[0002]

The fossil fuel supply uncertainty and the global warming due to carbon dioxide emission are becoming more serious. As a solution to the problems, biodiesel fuels derived from bioresources (biomass) begin to become widely available. The biodiesel fuels give a large amount of glycerol as a by-product in their production process. However, no effective method for utilizing glycerol has yet been established. This strongly necessitates a method for

converting glycerol into a useful compound to be used.

[0003]

Known glycerol conversion reactions include a hydrogenolysis reaction. The hydrogenolysis reaction converts glycerol into a mixture typically of 1,2-propanediol, 1,3-propanediol, ethylene glycol, and ethanol. Among them, 1,3-propanediol is particularly useful as a starting material for the production of polymers such as poly(trimethylene terephthalate)s (PTTs). This necessitates methods for producing 1,3-propanediol from glycerol selectively in a high yield.

[0004]

In a known method for producing 1,3-propanediol from glycerol selectively in a high yield (Non Patent Literature (NPL) 1), a catalyst including iridium and rhenium supported on silica is used in combination with a liquid acid catalyst (e.g., sulfuric acid). The liquid acid catalyst is used for better yield. Disadvantageously, however, the liquid acid catalyst (e.g., sulfuric acid), when used, adds constraints to a reactor to be used and increases the installation cost. Further disadvantageously, the method requires the removal of the liquid acid catalyst (e.g., sulfuric acid) from a product after the reaction, and this causes the production processes to be complicated.

[0005]

In known methods without using the liquid acid catalyst (e.g., sulfuric acid), a catalyst including platinum and tungstic acid supported on alumina is used (Patent Literature (PTL) 1, PTL 2, NPL 2, and NPL 3). Unfortunately, however, the catalyst in these methods has insufficient activity, low selectivity, and a short life.

Citation List

Patent Literature

[0006]

PTL 1: Japanese Unexamined Patent Application
Publication (JP-A) No. 2008-143798

PTL 2: JP-A No. 2007-326849

Non Patent Literature

[0007]

NPL 1: *Applied Catalysis B. Environmental* 105, 117
(2011)

NPL 2: *Catalysis Communications* 9, 1360 (2008)

NPL 3: *Green Chemistry* 12, 1466 (2010)

Summary of Invention

Technical Problem

[0008]

Accordingly, it is an object of the present invention to provide a catalyst for polyhydric alcohol hydrogenolysis, where the catalyst enables selective and high-yield

production of a corresponding hydrogenolysate from a polyhydric alcohol even without using a liquid acid catalyst; and in addition the catalyst is reusable and has a long life. It is another object of the present invention to provide a method for producing 1,3-propanediol from glycerol using the catalyst.

Solution to Problem

[0009]

After intensive investigations to achieve the objects, the present inventors have found a catalyst including a platinum component and a tungsten component both supported by boehmite; and have found that this catalyst enables efficient production of a corresponding hydrogenolysate from a polyhydric alcohol even without using a liquid acid catalyst. In addition, the present inventors have found that the catalyst, when used, enables selective and high-yield production of 1,3-propanediol from glycerol. The present invention has been made based on these findings.

[0010]

Specifically, the present invention provides, in an aspect, a catalyst for polyhydric alcohol hydrogenolysis. The catalyst includes boehmite $[AlO(OH)]$, a platinum component, and a tungsten component. The boehmite acts as a carrier and supports the platinum component and the tungsten component.

[0011]

A ratio (by weight, on metals basis) of the platinum component to the tungsten component contained in the catalyst is preferably from 1:0.05 to 1:50.

[0012]

The catalyst for polyhydric alcohol hydrogenolysis is preferably one obtained by allowing boehmite $[AlO(OH)]$ as the carrier to support the platinum component and the tungsten component, and thereafter performing firing at 200°C to 1000°C for 1 to 5 hours.

[0013]

In addition and advantageously, the present invention provides, in another aspect, a method for producing 1,3-propanediol. The method includes performing the hydrogenolysis of glycerol in the presence of hydrogen and the catalyst for polyhydric alcohol hydrogenolysis to give 1,3-propanediol.

[0014]

The hydrogenolysis is preferably performed in the presence of a solvent containing water.

Advantageous Effects of Invention

[0015]

The catalyst for polyhydric alcohol hydrogenolysis according to the present invention is hereinafter also simply referred to "the catalyst according to the present

invention". The catalyst according to the present invention, as having the configuration, can satisfactorily effectively promote the hydrogenolysis of a polyhydric alcohol and enables efficient hydrogenolysis of a polyhydric alcohol even without the combination use of a liquid acid catalyst (e.g., sulfuric acid). Typically, the catalyst, when used in the hydrogenolysis of glycerol, enables selective and extremely-high-yield production of 1,3-propanediol. In addition, the catalyst according to the present invention is reusable and can maintain its high catalytic activity even upon repetitive use. The catalyst can therefore contribute to reduced production cost of the hydrogenolysate and is extremely advantageous in industrialization.

The method for producing 1,3-propanediol according to the present invention using the catalyst for polyhydric alcohol hydrogenolysis can employ, as a reactor, a known or common one and does not have to select and uses a reactor made of an acid-resistant material. In an embodiment, the production method is performed without using an acid catalyst (e.g., sulfuric acid). The production method in this embodiment can omit the step of removing the acid catalyst (e.g., sulfuric acid) from a reaction product after the reaction, and this can simplify the production process. In addition, the method for producing 1,3-propanediol according to the present invention can produce useful 1,3-

propanediol efficiently and selectively from glycerol, where the glycerol is by-produced in the production process of biodiesel fuels. Thus, the production method can effectively utilize bioresources and can reduce the emissions of carbon dioxide that may cause global warming.

Description of Embodiments

[0016]

Catalyst for Polyhydric Alcohol Hydrogenolysis

The catalyst according to the present invention includes boehmite $[\text{AlO}(\text{OH})]$, a platinum component, and a tungsten component. The boehmite acts as a carrier and supports the platinum component and the tungsten component.

[0017]

The platinum component may be supported in an amount (on metals basis) of typically from about 0.005 to about 0.3 mmol, preferably from 0.01 to 0.2 mmol, and particularly preferably from 0.05 to 0.15 mmol, per 1 g of the boehmite. The platinum component, if supported in an amount less than the range, may tend to cause a lower conversion from glycerol. In contrast, the platinum component, if supported in an amount greater than the range, may cause economical disadvantages.

[0018]

The tungsten component may be supported in an amount (on metals basis) of typically from about 0.05 to about 15

mmol, preferably from 0.1 to 10 mmol, particularly preferably from 0.4 to 5 mmol, and most preferably from 0.4 to 3 mmol, per 1 g of the boehmite. The tungsten component, if supported in an excessively large amount, may readily cover the entire surface of the boehmite and restrain the boehmite from exhibiting its effects (e.g., glycerol adsorption effect). This may readily cause a lower conversion from glycerol. In contrast, the tungsten component, if supported in an excessively small amount, may readily fail to exhibit its effects (e.g., reaction promoting effect).

[0019]

The platinum component and the tungsten component may be supported in such amounts (on metals basis) that the ratio (by weight) of the platinum component to the tungsten component is typically from 1:0.05 to 1:50, preferably from 1:0.1 to 1:10, and particularly preferably from 1:3 to 1:5. The platinum component and the tungsten component, if supported in a ratio out of the range, may readily cause a lower conversion from glycerol.

[0020]

The boehmite is alumina monohydrate represented by the chemical composition of $\text{AlO}(\text{OH})$. The boehmite may be produced typically by subjecting alumina trihydrate to heat treatment or hydrothermal treatment each in the air.

[0021]

The boehmite may be in the form typically of a powder, granule, or molded article. Among them, boehmite in the form of a powder is preferably used herein. The boehmite may have an average pore diameter of typically from about 1 to about 20 nm, and preferably from 5 to 10 nm. The boehmite may have a specific surface area of typically from about 100 to about 400 m²/g, and preferably from 150 to 300 m²/g.

[0022]

The boehmite for use in the present invention may also be selected from commercial products available typically under the trade names of: Boehmite (from Wako Pure Chemical Industries, Ltd.), Boehmite (from TAIMEI CHEMICALS CO., LTD.), and boehmite (from Sigma-Aldrich Co. LLC.).

[0023]

The platinum component and the tungsten component to be supported by the boehmite may each be in any form not critical, such as forms of elemental metals, metal salts, metal oxides, metal hydroxide, and metal complexes. The platinum component for use herein is preferably supported in the form of an elemental metal. This is preferred so as to allow the reaction to proceed efficiently. The platinum component may have an average particle diameter of typically from about 0.9 to about 10 nm, and preferably from 1 to 5 nm.

The platinum component, if having an average particle diameter of greater than the range, may readily cause the catalyst to have lower reactivity. The tungsten component is preferably in the form of an oxide (in particular, tungsten trioxide). This is preferred for the development of high catalytic activity. As used herein the term "average particle diameter" refers to an average of equivalent circle diameters determined based on a transmission electron photomicrograph.

[0024]

A way to allow the boehmite to support the platinum component and the tungsten component is not limited and may be selected from known or common supporting methods. In particular, the supporting in the present invention is preferably performed by a so-called impregnation method. In the impregnation method, boehmite is impregnated with a solution containing a platinum compound and another solution containing a tungsten compound, then dried, and fired. The platinum compound is exemplified by H_2PtCl_6 , $(\text{NH}_4)_2\text{PtCl}_6$, and K_2PtCl_6 . The tungsten compound is exemplified by ammonium paratungstate $[(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}]$, ammonium metatungstate, and sodium tungstate. In a preferred embodiment, the amounts of the platinum component and the tungsten component to be supported are controlled by adjusting the concentrations of the two solutions respectively containing

the platinum compound and the tungsten compound, and the impregnation time of the boehmite. The impregnation with the two solutions respectively containing the platinum compound and the tungsten compound, and the drying of the carrier impregnated with the solutions may be performed independently at a temperature not critical.

[0025]

The boehmite may be impregnated with the solution containing the platinum compound and the solution containing the tungsten compound simultaneously or sequentially. Specifically, in an embodiment, the boehmite is impregnated with the solution containing the tungsten compound and thereafter impregnated with the solution containing the platinum compound. In another embodiment, the boehmite is impregnated with the solution containing the platinum compound and thereafter impregnated with the solution containing the tungsten compound. In still another embodiment, the boehmite is impregnated simultaneously with the solution containing the platinum compound and the solution containing the tungsten compound.

[0026]

In particular in the present invention, preferred are catalysts obtained by a method in which the boehmite is impregnated with the solution containing the tungsten compound and thereafter impregnated with the solution

containing the platinum compound. Among them, particularly preferred are catalysts obtained by a method in which the boehmite is impregnated with the solution containing the tungsten compound, dried, and fired, and thereafter impregnated with the solution containing the platinum compound, dried, and fired. These catalysts are preferred because the platinum component acting as a catalytic substance is exposed from the surface in a larger amount, and this enables efficient conversion from glycerol and selective formation of 1,3-propanediol.

[0027]

The solution containing the platinum compound may have a concentration of typically from about 0.5 to about 20 mmol/L, preferably from 1 to 10 mmol/L, and particularly preferably from 1 to 5 mmol/L. The solution containing the platinum compound, if having a concentration of less than the range, may cause the carrier (boehmite) to support a smaller amount of the platinum component to cause the catalyst to offer a lower conversion from glycerol. In contrast, the solution containing the platinum compound, if having a concentration of greater than the range, may cause economical disadvantages.

[0028]

The impregnation of the boehmite with the solution containing the platinum compound may be performed for a time

(duration) of typically from about 1 to about 24 hours, and preferably from 10 to 20 hours. The impregnation, if performed for a time shorter than the range, may cause the carrier to support a smaller amount of the platinum component and may readily cause the catalyst to offer a lower conversion from glycerol.

[0029]

The solution containing the tungsten compound may have a concentration of typically from about 1 to about 100 mmol/L, preferably from 1 to 50 mmol/L, and particularly preferably from 1 to 20 mmol/L. The solution containing the tungsten compound, if having a concentration of less than the range, may cause the carrier to support a smaller amount of tungsten. In contrast, the solution containing the tungsten compound, if having a concentration of greater than the range, may cause economical disadvantages.

[0030]

The impregnation of the boehmite with the solution containing the tungsten compound may be performed for a time (duration) of typically from about 1 to about 24 hours, and preferably from 10 to 20 hours. The impregnation, if performed for a time longer than the range, may cause the tungsten component to cover the entire surface of the boehmite and may restrain the boehmite from exhibiting its effects (e.g., glycerol adsorption effect). This may

readily cause a lower conversion from glycerol. In contrast, the impregnation, if performed for a time shorter than the range, may cause the carrier to support a smaller amount of the tungsten component, and this may readily cause the tungsten component to hardly exhibit its effects (e.g., reaction promoting effect).

[0031]

In an embodiment, the boehmite is impregnated with the solution containing the tungsten compound, dried, and fired before being impregnated with the solution containing the platinum compound. In this embodiment, the firing of the dried boehmite may be performed at a temperature of typically from about 100°C to about 1000°C, preferably from 500°C to 1000°C, and particularly preferably from 700°C to 900°C in the air for a firing time of typically from about 0.5 to about 10 hours, and preferably from 1 to 5 hours. The firing may be performed in an atmosphere that is not limited to the air and is exemplified by nitrogen, argon, or another inert gas atmosphere; and hydrogen or another reducing gas atmosphere.

[0032]

In an embodiment, the boehmite is impregnated with the two solutions respectively containing the platinum compound and the tungsten compound, dried, and fired. In this embodiment, the firing of the dried boehmite may be

performed at a temperature of typically from about 200°C to about 1000°C, preferably from 200°C to 600°C, and particularly preferably from 200°C to 400°C in the air. The firing, if performed at an excessively high temperature, may readily cause the supported platinum component to aggregate and to be dispersed unsatisfactorily. This may cause the catalyst to have lower reactivity. The firing may be performed for a time of from about 1 to about 5 hours. The firing may be performed in an atmosphere that is not limited to the air and is exemplified by nitrogen, argon, or another inert gas atmosphere; and hydrogen or another reducing gas atmosphere.

[0033]

After the firing, the catalyst according to the present invention may further be subjected to reduction treatment. A reducing agent for use in the catalyst reduction treatment is exemplified by borohydride complex compounds such as sodium borohydride (NaBH_4), lithium borohydride (LiBH_4), and potassium borohydride (KBH_4); hydrazine; hydrogen (H_2); silane compounds such as dimethylphenylsilane; and hydroxy compounds. The hydroxy compounds are exemplified by alcohol compounds such as primary alcohols and secondary alcohols. The hydroxy compounds may be any of monohydric alcohols, dihydric alcohols, and polyhydric alcohols (e.g., glycerol).

[0034]

Among them, hydrogen (H_2) and glycerol are preferably used as the reducing agent for use in the reduction treatment of the catalyst according to the present invention. This allows the reduction treatment to be performed simultaneously with the glycerol hydrogenolysis reaction.

[0035]

The reduction treatment may be performed at a temperature of typically from $100^{\circ}C$ to $600^{\circ}C$ (and preferably from $150^{\circ}C$ to $400^{\circ}C$) for a time of typically from about 0.5 to about 5 hours (and preferably from 2 to 4 hours).

[0036]

The catalyst obtained by the production method may be subjected to washing treatment and/or drying treatment. In the washing treatment, the catalyst is washed typically with water and/or an organic solvent. In the drying treatment, the catalyst is dried typically by vacuum drying.

[0037]

The catalyst according to the present invention is useful as a catalyst for polyhydric alcohol hydrogenolysis. The polyhydric alcohol is exemplified by glycerol, 1,3-propanediol, 1,2-propanediol, 2,3-butanediol, and 1,2-butanediol. In particular, the catalyst according to the present invention may be used as a catalyst preferably for the hydrogenolysis of glycerol, 1,3-propanediol, and 1,2-propanediol, more preferably for the hydrogenolysis of

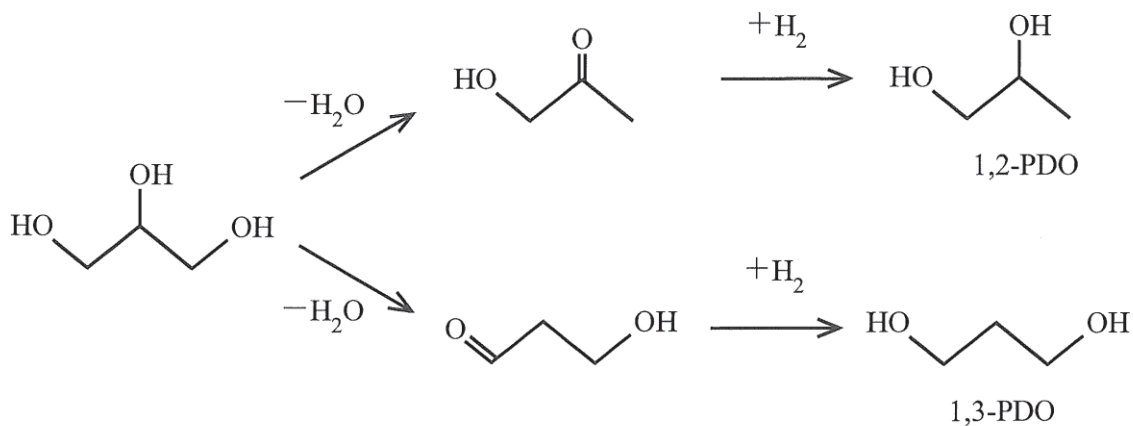
glycerol and 1,2-propanediol, and particularly preferably for the hydrogenolysis of glycerol.

[0038]

In the hydrogenolysis of glycerol using the catalyst according to the present invention, a reaction proceeds probably in a manner below. To form 1,3-propanediol selectively, there is a need for allowing a dehydration reaction to selectively occur in a secondary hydroxy group. The catalyst according to the present invention includes boehmite as the carrier, and the platinum component in combination with the tungsten component both supported on the carrier. The catalyst thereby enables the control of variations in acidity of the carrier to allow the dehydration reaction to proceed more selectively in the secondary hydroxy group. This probably enables the selective formation of 1,3-propanediol.

[0039]

[Chem. 1]



[0040]

Likewise, the catalyst according to the present invention, when used in a hydrogenolysis reaction of 1,2-propanediol, enables selective dehydration of a secondary hydroxy group to form 1-propanol selectively.

[0041]

Method for Producing 1,3-Propanediol

The method for producing 1,3-propanediol according to the present invention includes performing hydrogenolysis of glycerol in the presence of hydrogen and the catalyst for polyhydric alcohol hydrogenolysis to give 1,3-propanediol.

[0042]

The catalyst may undergo a reduction treatment before use or may be subjected to a reduction treatment in the reaction system.

[0043]

The catalyst may be used in an amount of typically from

about 0.01 to about 1 g, preferably from 0.03 to 0.5 g, and particularly preferably from 0.05 to 0.2 g, per 1 mmol of glycerol.

[0044]

The hydrogen may be supplied typically by performing the reaction in the presence of hydrogen (specifically, in a hydrogen atmosphere); or by bubbling hydrogen gas. The hydrogen (hydrogen gas) may include approximately hydrogen alone, or may be diluted typically with an inert gas such as nitrogen, argon, or helium. The hydrogen for use herein may also be recycled hydrogen that is recovered from a reaction mixture obtained by the method for producing 1,3-propanediol according to the present invention.

[0045]

The reaction, when performed in hydrogen, may be performed at a hydrogen pressure of typically from about 10 to about 80 atm (atmospheres), and preferably from 30 to 60 atm.

[0046]

The molar ratio [hydrogen (mol)/glycerol (mol)] of hydrogen to glycerol to be subjected to the reaction is typically from about 1 to about 200, preferably from 50 to 150, and particularly preferably from 60 to 120. The reaction, if performed at a molar ratio of hydrogen to glycerol of less than the range, may cause a lower

conversion (rate of conversion) from glycerol. In contrast, the reaction, if performed at a molar ratio of hydrogen to glycerol of greater than the range, may readily cause increased utility cost for the recovery of unreacted hydrogen.

[0047]

The reaction may be performed according to a system optionally selected typically from batch, semi-batch, and continuous flow systems. In a preferred embodiment of the method, unreacted glycerol after the hydrogenolysis is separated, recovered, and recycled. This is preferred for the production of a larger amount of 1,3-propanediol from a predetermined amount of glycerol.

[0048]

The reaction is preferably performed in the presence of a solvent. This is because the reaction, if performed in the absence of a solvent, may cause the substrate glycerol to be adsorbed by the catalyst to form a lump, and this may impede the reaction progress. The solvent is exemplified by water; alcohols such as methanol and ethanol; ethers such as 1,2-dioxane, 1,3-dioxane, 1,4-dioxane, tetrahydrofuran, tetrahydropyran, diethyl ether, and dimethyl ether; amides such as acetamide, dimethylacetamide, dimethylformamide, diethylformamide, and N-methylpyrrolidone; esters such as ethyl acetate, propyl acetate, and butyl acetate; and

mixtures of them.

[0049]

Of such solvents for use herein, solvents containing water are preferred so as to form 1,3-propanediol selectively in a good yield. More preferred as the solvent is water alone or a solvent mixture containing water and an alcohol in a proportion of less than 1 mL per 1 mL of water. The solvent mixture more preferably contains water and an alcohol in a proportion of 0.5 mL or less per 1 mL of water. In an embodiment, the reaction is performed in a batch system. In this embodiment, the solvent may be used in an amount within such a range that the initial concentration of glycerol be from about 1 to about 60 percent by weight.

[0050]

The reaction may be performed at a temperature of typically from about 50°C to about 250°C, preferably from 100°C to 220°C, and particularly preferably from 150°C to 200°C. The reaction may be performed for a time of typically from about 1 to about 24 hours, and preferably from 5 to 15 hours, while the reaction time may be adjusted as appropriate with reference to the reaction temperature and pressure. The reaction, if performed for a time shorter than the range, may cause a lower conversion (rate of conversion) from glycerol. In contrast, the reaction, if performed for a time longer than the range, may cause

abruptly increased formation of a hydrocarbon as a complete hydrogenolysate of glycerol.

[0051]

After the completion of the reaction, a reaction product may be separated/purified by a separation method such as filtration, concentration, distillation, or extraction, or a separation method as any combination of them.

[0052]

The method for producing 1,3-propanediol according to the present invention performs the hydrogenolysis of glycerol to convert glycerol with a good conversion to produce 1,3-propanediol selectively. The conversion from glycerol is typically 10% or more, preferably 25% or more, more preferably 40% or more, furthermore preferably 50% or more, particularly preferably 70% or more, and most preferably 80% or more. The selectivity for 1,3-propanediol is typically 20% or more, preferably 40% or more, more preferably 50% or more, furthermore preferably 60% or more, and particularly preferably 65% or more.

[0053]

The method for producing 1,3-propanediol according to the present invention allows the hydrogenolysis reaction of glycerol to be performed under mild conditions. The method can convert glycerol with a good conversion to produce 1,3-

propanediol selectively even using approximately no liquid acid catalyst (e.g., sulfuric acid). The amount of the liquid acid catalyst (e.g., sulfuric acid) herein may typically be 100 ppm or less. The method can employ, as a reactor, a known or common one and does not have to select and use a reactor of an acid-resistant material. In an embodiment, the method does not employ the liquid acid catalyst (e.g., sulfuric acid). In this embodiment, the method can omit the step of removing the liquid acid catalyst (e.g., sulfuric acid) from the reaction product after the reaction, and this can simplify production processes.

[0054]

The catalyst according to the present invention can maintain its high catalytic activity even upon repetitive use and regeneration. The catalyst used in the reaction can be easily recovered from the reaction mixture by a physical separation technique such as filtration and/or centrifugal separation, and the recovered catalyst may be reused as intact (without treatment) or after being subjected to treatment such as washing, drying, and/or firing. The firing treatment herein may be performed at a temperature of about 300°C. The washing treatment may be performed typically by washing the catalyst with an appropriate solvent (e.g., water) several times (about two or about

three times). This enables repetitive use of the expensive catalyst to significantly reduce the production cost of 1,3-propanediol.

Examples

[0055]

The present invention will be illustrated in further detail with reference to several examples below. It should be noted, however, that the examples are by no means intended to limit the scope of the present invention. In tables below, the symbols "Gly", "1,3-PDO", "1,2-PDO", "2-PO", and "1-PO" respectively represent glycerol, 1,3-propanediol, 1,2-propanediol, 2-propanol, and 1-propanol.

[0056]

Preparation Example 1: Catalyst preparation

A catalyst was prepared by the impregnation method. Specifically, 20 g of boehmite was added to an aqueous ammonium paratungstate solution (1) and stirred for 16 hours. After distilling off water on an evaporator, the residue was dried, fired at 800°C for 3 hours, and yielded a tungsten-supported boehmite. The boehmite was a product supplied under the trade name of Boehmite by Wako Pure Chemical Industries, Ltd. and having an average pore diameter of 77 nm and a specific surface area of 214 m²/g. The aqueous ammonium paratungstate solution (1) was a solution containing 2 g (0.65 mmol) of (NH₄)₁₀H₂(W₂O₇)₆•xH₂O (supplied

by Sigma-Aldrich Co. LLC.) in 200 mL of water.

Next, 2 g of the above-prepared tungsten-supported boehmite was added to an aqueous chloroplatinic acid solution (1) and stirred for 12 hours. The aqueous chloroplatinic acid solution (1) was a solution containing 4 mL (0.2 mmol in terms of H_2PtCl_6) of 2 percent by weight aqueous chloroplatinic acid solution diluted with 100 mL of deionized water.

After the completion of stirring, water was distilled off on an evaporator, the residue was dried, fired at 300°C for 3 hours, and yielded a catalyst (1). The catalyst (1) included a platinum component and a tungsten component supported by boehmite and had a platinum (Pt) content of 2 percent by weight, an average particle diameter of the platinum component of 2 nm, and a tungsten (W) content of 8 percent by weight. The average particle diameter of the platinum component was an average of equivalent circle diameters of platinum component particles determined based on a transmission electron photomicrograph.

The catalyst (1) was subjected to X-ray diffractometry to find that no peak assigned to platinum and tungsten trioxide was detected. This demonstrates that platinum and tungsten trioxide were highly dispersed and supported on the carrier surface.

[0057]

Preparation Example 2: Catalyst preparation

A catalyst (2) having a platinum content of 1 percent by weight and a tungsten content of 8 percent by weight was prepared by the procedure of Preparation Example 1, except for using an aqueous chloroplatinic acid solution (2), instead of the aqueous chloroplatinic acid solution (1). The aqueous chloroplatinic acid solution (2) was a solution containing 2 mL (0.1 mmol in terms of H_2PtCl_6) of 2 percent by weight aqueous chloroplatinic acid solution diluted with 100 mL of deionized water.

[0058]

Preparation Example 3: Catalyst preparation

A catalyst (3) having a platinum content of 1 percent by weight and a tungsten content of 8 percent by weight was prepared by the procedure of Preparation Example 2, except for performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours.

[0059]

Preparation Example 4: Catalyst preparation

A catalyst (4) having a platinum content of 5 percent by weight and a tungsten content of 8 percent by weight was prepared by the procedure of Preparation Example 1, except for using an aqueous chloroplatinic acid solution (3) instead of the aqueous chloroplatinic acid solution (1). The aqueous chloroplatinic acid solution (3) was a solution

containing 10 mL (0.5 mmol in terms of H_2PtCl_6) of 2 percent by weight aqueous chloroplatinic acid solution diluted with 100 mL of deionized water.

[0060]

Preparation Example 5: Catalyst preparation

A catalyst (5) having a platinum content of 2 percent by weight and a tungsten content of 10 percent by weight was prepared by the procedure of Preparation Example 1, except for adding boehmite in an amount of 5 g to an aqueous ammonium paratungstate solution (2) instead of the aqueous ammonium paratungstate solution (1), and performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours. The aqueous ammonium paratungstate solution (2) was a solution of 0.998 g (0.326 mmol) of $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$ (supplied by Sigma-Aldrich Co. LLC.) in 100 mL of water.

[0061]

Preparation Example 6: Catalyst preparation

A catalyst (6) having a platinum content of 2 percent by weight and a tungsten content of 24 percent by weight was prepared by the procedure of Preparation Example 1, except for using an aqueous ammonium paratungstate solution (3) instead of the aqueous ammonium paratungstate solution (1), and performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours. The aqueous

ammonium paratungstate solution (3) was a solution of 2.495 g (0.815 mmol) of $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$ (supplied by Sigma-Aldrich Co. LLC.) in 100 mL of water.

[0062]

Preparation Example 7: Catalyst preparation

A catalyst (7) having a platinum content of 2 percent by weight and a tungsten content of 64 percent by weight was prepared by the procedure of Preparation Example 1, except for adding 5 g of boehmite to an aqueous ammonium paratungstate solution (4) instead of the aqueous ammonium paratungstate solution (1), and performing firing at 300°C for 3 hours after this impregnation. The aqueous ammonium paratungstate solution (4) was a solution of 24.819 g (8.1 mmol) of $(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$ (supplied by Sigma-Aldrich Co. LLC.) in 100 mL of water.

[0063]

Preparation Example 8: Catalyst preparation

A catalyst (8) having a platinum content of 2 percent by weight and a tungsten content of 64 percent by weight was prepared by the procedure of Preparation Example 7, except for performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours.

[0064]

Preparation Example 9: Catalyst preparation

A catalyst (9) having a platinum content of 1 percent

by weight and a tungsten content of 10 percent by weight was prepared by the procedure of Preparation Example 1, except for using the aqueous ammonium paratungstate solution (2) and the aqueous chloroplatinic acid solution (2) respectively instead of the aqueous ammonium paratungstate solution (1) and the aqueous chloroplatinic acid solution (1).

[0065]

Preparation Example 10: Catalyst preparation

A catalyst (10) having a platinum content of 1 percent by weight and a tungsten content of 10 percent by weight was prepared by the procedure of Preparation Example 9, except for performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours.

[0066]

Preparation Example 11: Catalyst preparation

A catalyst (11) having a platinum content of 5 percent by weight and a tungsten content of 10 percent by weight was prepared by the procedure of Preparation Example 1, except for using the aqueous ammonium paratungstate solution (2) and the aqueous chloroplatinic acid solution (3) respectively instead of the aqueous ammonium paratungstate solution (1) and the aqueous chloroplatinic acid solution (1), and performing firing at 500°C for 3 hours after the impregnation, instead of at 300°C for 3 hours.

[0067]

Example 1

In a 50-mL stainless autoclave including a TeflonTM inner cylinder, 0.1 g of the catalyst (1) (Pt-W/AlO(OH), having a platinum content of 2 percent by weight and a tungsten content of 8 percent by weight) prepared in Preparation Example 1, 1 mmol of glycerol, and 3.0 mL of water were placed, stirred at 180°C in a hydrogen atmosphere (50 atm: 120 mol of H₂ per 1 mol of glycerol) for 12 hours, and yielded a product. The conversion, selectivity, and yield herein were measured using a gas chromatograph-mass spectrometer (GC-MS).

[0068]

Examples 2 to 11

Products were obtained by the procedure of Example 1, except for using catalysts indicated in Table 1, instead of the catalyst (1) prepared in Preparation Example 1.

[0069]

[Table 1]

TABLE 1

	Catalyst number	Gly Conv (%)	Yield (%) (Selectivity (%))				
			1,3-PDO	1,2-PDO	2-PO	1-PO	Others
Example 1	Catalyst (1)	100	65.7 (65.7)	2.2 (2.2)	5.5 (5.5)	10.7 (10.7)	15.9
Example 2	Catalyst (2)	31.27	23.42 (74.92)	2.82 (9.38)	1.69 (5.62)	1.06 (3.52)	1.69
Example 3	Catalyst (3)	83.37	43.53 (52.22)	5.59 (6.73)	4.02 (4.83)	13.98 (16.81)	16.26
Example 4	Catalyst (4)	86.79	41.2 (47.47)	3.53 (4.08)	7.65 (8.83)	22.57 (26.07)	11.84
Example 5	Catalyst (5)	49.6	26.2 (52.9)	4.0 (8.2)	4.7 (9.6)	10.7 (21.9)	3.99
Example 6	Catalyst (6)	25.78	18.72 (72.59)	3.17 (12.82)	1.51 (6.1)	4.68 (18.92)	-
Example 7	Catalyst (7)	12.6	6.9 (54.6)	-	-	-	5.7
Example 8	Catalyst (8)	17.1	10.3 (60.3)	1.67 (10.5)	0.85 (5.3)	2.62 (16.42)	1.66
Example 9	Catalyst (9)	46.97	19.35 (41.2)	2.81 (5.98)	2.04 (4.34)	10.03 (21.35)	12.74
Example 10	Catalyst (10)	36.96	21.82 (70.49)	3.74 (12.53)	2.42 (8.11)	4.03 (13.51)	4.95
Example 11	Catalyst (11)	57.28	31.37 (54.77)	5.39 (9.54)	3.21 (5.67)	16.88 (29.8)	0.46

[0070]

Examples 12 and 13

Products were obtained by the procedure of Example 1, except for using, instead of water, solvents indicated in Table 2 below.

[0071]

[Table 2]

TABEL 2

	Solvent	Gly Conv (%)	Yield (%) (Selectivity (%))					1,3-PDO/1,2-PDO (Molar ratio)
			1,3-PDO	1,2-PDO	2-PO	1-PO	Others	
Example 1	Water	100	65.7 (65.7)	2.2 (2.2)	5.5 (5.5)	10.7 (10.7)	15.9	29.85
Example 12	Ethanol	32	1.7 (5.3)	4.0 (12.5)	3.4 (10.6)	17.2 (53.75)	5.7	0.425
Example 13	Water-Ethanol (2 mL:1 mL)	45	10.2 (22.7)	3.1 (6.89)	4.0 (8.89)	25.9 (57.6)	1.8	3.3

[0072]

Referential Examples 1 and 2

Products were obtained by the procedure of Example 1, except for using, instead of glycerol, reaction substrates indicated in Table 3 below.

[0073]

[Table 3]

TABLE 3

	Substrate	Gly Conv (%)	Yield (%) (Selectivity (%))				
			1,3-PDO	1,2-PDO	2-PO	1-PO	Others
Example 1	Glycerol	100	65.7 (65.7)	2.2 (2.2)	5.5 (5.5)	10.7 (10.70)	15.9
Referential Example 1	1,2-PDO	99.5	-	-	17.9 (17.9)	79.9 (80.2)	1.7
Referential Example 2	1,3-PDO	27	-	-	-	20.9 (77.4)	6.1

Industrial Applicability

[0074]

The catalyst for polyhydric alcohol hydrogenolysis according to the present invention, as having the configuration, satisfactorily effectively promotes the

hydrogenolysis of a polyhydric alcohol and enables efficient hydrogenolysis of a polyhydric alcohol even when used without the combination use of a liquid acid catalyst (e.g., sulfuric acid). Typically, the catalyst, when used in hydrogenolysis of glycerol, enables selective and extremely-high-yield production of 1,3-propanediol. In addition, the catalyst according to the present invention is reusable and can maintain its high catalytic activity even upon repetitive use. The catalyst can therefore contribute to reduced cost for the production of a hydrogenolysate and is extremely advantageous in industrialization.

The method for producing 1,3-propanediol according to the present invention using the catalyst for polyhydric alcohol hydrogenolysis can employ, as a reactor, a known or common one without the need for selecting and using a reactor made of an acid-resistant material. In an embodiment, the production method is performed without using an acid catalyst (e.g., sulfuric acid). The production method in this embodiment can omit the step of removing the acid catalyst (e.g., sulfuric acid) from a reaction product after the reaction, and this can simplify the production process. In addition, the method for producing 1,3-propanediol according to the present invention can produce useful 1,3-propanediol efficiently and selectively from glycerol, where the glycerol is by-produced in the

production process of biodiesel fuels. Thus, the production method can effectively utilize bioresources and can reduce the emissions of carbon dioxide that causes global warming.

CLAIMS

[Claim 1]

A catalyst for polyhydric alcohol hydrogenolysis, the catalyst comprising:

boehmite $[AlO(OH)]$ as a carrier;

a platinum component; and

a tungsten component,

the platinum component and the tungsten component being supported by the boehmite carrier.

[Claim 2]

The catalyst for polyhydric alcohol hydrogenolysis according to claim 1,

wherein a ratio (by weight, on metals basis) of the platinum component to the tungsten component is from 1:0.05 to 1:50.

[Claim 3]

The catalyst for polyhydric alcohol hydrogenolysis according to one of claims 1 and 2,

wherein the catalyst is obtained by:

a) allowing boehmite $[AlO(OH)]$ as the carrier to support the platinum component and the tungsten component; and

b) performing firing at 200°C to 1000°C for 1 to 5 hours after the step a).

[Claim 4]

A method for producing 1,3-propanediol, the method comprising

performing hydrogenolysis of glycerol in the presence of hydrogen and the catalyst for polyhydric alcohol hydrogenolysis according to any one of claims 1 to 3 to give 1,3-propanediol.

[Claim 5]

The method for producing 1,3-propanediol, according to claim 4,

wherein the hydrogenolysis is performed in the presence of a solvent comprising water.