

Catalyst for Producing Isopropylbenzene and the Production Method and Use thereof

5

Technical Field

This invention relates to a catalyst for producing isopropylbenzene, in particular, to a catalyst for producing isopropylbenzene by using α,α -dimethylbenzyl alcohol (DMBA), and the production method and use
10 thereof.

Background Art

Propylene oxide (PO for short) is an important organic industrial chemical material which is mainly used for producing polyether polyols, propylene glycols, propanediol ethers, etc., wherein the consumption of polyether
15 polyols accounts for about 70%. At present, commercialized processes for the production of PO mainly include chlorohydrin process, co-oxidation process (PO/SM) and isopropylbenzene hydroperoxide recycling process (CHP). The CHP process has the following advantages: the conversion and the selectivity of the whole process are very high; the process leads to the
20 only product of PO and is not affected by the price fluctuation of by-product of styrene, as can bring more stable economic benefits to manufacturers; the technological process is relatively simple, where the fixed investment is two thirds as much as that of the PO/SM process. Furthermore the requirements for anti-corrosion on devices in the CHP
25 process are relatively low. In the technique for the production of propylene oxide by CHP process, a large amount of α,α -dimethylbenzyl alcohol (DMBA) is generated in the process of propylene epoxidation. The α,α -dimethylbenzyl alcohol needs to be hydrogenated to produce isopropylbenzene to re-participate in the reaction cycle.

30 US patent US6646139B2 provides a process for producing

isopropylbenzene by the catalytic hydrogenolysis of α,α -dimethylbenzyl alcohol with H_2 as a hydrogen source and copper-Cr as a catalyst. Although the conversion of α,α -dimethylbenzyl alcohol can be up to 99%, the selectivity is less than 98%. Moreover, the use of element Cr in the
5 production of the catalyst results in a serious environmental pollution. Chinese patent CN101733093 B reported that the reaction of alumina-supported or zeolite-supported metal palladium or a mixture of palladium and Pt at a reaction temperature lower than 160 °C achieved a conversion of α,α -dimethylbenzyl alcohol greater than 99.5% and a
10 selectivity of isopropylbenzene greater than 99.5%. The stronger acidity of the support in the patent significantly led to the polymerization of methylstyrene-an intermediate product of dehydration of α,α -dimethylbenzyl alcohol. The patent does not mention the technical problem of stability of the catalyst. Chinese patent application
15 CN104230640 A points out that use of a palladium/ SiO_2 catalyst can realize 100% conversion of α,α -dimethylbenzyl alcohol but a selectivity of isopropylbenzene lower than 98.5% under reaction temperature of 180°C.

A well-known method for producing isopropylbenzene is dehydrating cumyl alcohol to alpha-methyl styrene in the presence of a dehydration catalyst,
20 and hydrogenating the alpha-methyl styrene to cumene in the presence of a hydrogenation catalyst (for example, European Chemical News Volume 74 Number 19475-11 March 2001). Chinese patent CN1732139A discloses providing cumyl alcohol and hydrogen to a dehydration catalyst to obtain a mixture comprising the resultant alpha-methyl styrene and water and
25 hydrogen; providing the mixture to a hydrogenation catalyst, wherein the reaction temperature and pressure are so selected that the water contained in the α -methylstyrene solution after dehydration is not agglutinated. The reaction temperature is preferably 150 to 300°C, and the reaction pressure is preferably 100 to 2000kPa. When the temperature is lower than 150°C
30 and the pressure is higher than 2000kPa, water agglutination sometimes occurs at the dehydration reaction outlet, which degrades the performance

of the hydrogenation catalyst. However, the well-known method cannot meet the requirements of low-cost and efficient production of isopropylbenzene.

5 In the prior art, there are problems including the catalyst activity and selectivity needed to be further improved, the poor stability and the serious environmental pollution in the production of isopropylbenzene by catalyzing the dehydration and hydrogenation of α,α -dimethylbenzyl alcohol.

Contents of Invention

10 The present invention provides a highly active and highly selective supported palladium catalyst having an excellent catalytic activity and selectivity, an excellent hydration resistance and a good stability in order to solve the technical problems of low activity and selectivity, poor stability and serious environmental pollution of catalysts in the prior art.

15 One object of the present invention is to provide a catalyst for producing isopropylbenzene, in particular, a catalyst for producing isopropylbenzene from α,α -dimethylbenzyl alcohol, comprising a support and an active component supported on the support, wherein the support comprises a support substrate and a modifying auxiliary component supported on the
20 support substrate, wherein the active component includes metal palladium and/or oxides thereof, and the modifying auxiliary component includes phosphorus and/or oxides thereof.

The support substrate herein is not particularly limited and can be a common catalyst support in this field, unless otherwise specified. In a
25 preferred embodiment, the support substrate is at least one selected from the group consisting of silica, alumina and activated carbon, preferably alumina.

In a preferred embodiment, the support substrate has a pore size of

10-25nm and a specific surface area of 50-180m²/g; more preferably, the support substrate has a pore size of 12-18nm and a specific surface area of 120-160 m²/g.

5 In a preferred embodiment, the content of the metal palladium and/or oxides thereof in the catalyst is 0.01-5wt%. In a further preferred embodiment, the content of the metal palladium and/or oxides thereof in the catalyst is 0.05-1wt%, for example, 0.05-0.5wt%, wherein the content of the metal palladium and/or oxides thereof is based on the content of element palladium therein.

10 In the present invention, the source of the metal palladium is not particularly limited, preferably but not limited to at least one selected from the group consisting of palladium chloride, palladium nitrate and chloropalladic acid.

15 In a preferred embodiment, the catalyst has a palladium dispersity of 5-10%, preferably 6.5-8.5%.

Here, the hydrogenolysis of α,α -dimethylbenzyl alcohol is the coupling of two steps of dehydration and hydrogenation. Studies have found that dehydration is the determining step of the reaction. Therefore, we should first improve the dehydration activity of the catalyst in the regulation of the catalyst, so as to improve the reaction rate of the whole reaction. The dispersity of metal palladium has a certain relationship with its grain size. Generally, the larger the grain is, the lower the dispersity is. Studies also have found that the Pd dispersity is not in a linear relationship with the grain size because TEM analysis found that the grain size of Pd did not increase significantly on a catalyst having a reduced dispersity. In addition, an appropriate grain growth of a Pd catalyst is helpful to improve the reaction selectivity. Therefore, it is necessary to control the dispersity within a reasonable range.

The dispersity of metal Pd is determined by hydrogen-oxygen titration

method. The specific analysis steps include: raising the temperature of the catalyst to 120°C (heating rate 10 °C/min) in a certain hydrogen flow, the temperature retaining constant for 2 hours; then raising the temperature to 145°C, purging with argon for 1 hour and then lowering the temperature to room temperature (in argon atmosphere). Chemical adsorption of oxygen: at the room temperature, introducing oxygen by pulse to a sample tube until saturation; then purging with argon for 40 min. The determination of the amount of hydrogen titration: quantitative pulse of hydrogen is made with a six-way feeding valve (quantitative tube volume of 0.3mL). The amount of consumed hydrogen can be calculated based on the area difference between the front and rear peaks on the chromatographic instrument, so that the dispersity of metal Pd on the catalyst can be calculated.

In a preferred embodiment, the active component further includes an active auxiliary metal and/or oxides thereof. Preferably, the active auxiliary metal is at least one selected from the group consisting of metal copper, metal zinc, metal cobalt, metal tin, metal nickel and metal silver, for example, metal copper. In a further preferred embodiment, the content of the active auxiliary metal and/or oxides thereof in the catalyst is 0.0001-0.2wt%, preferably 0.0007-0.2wt%, wherein the content of the active auxiliary metal and/or oxides thereof is based on the content of the auxiliary metal element therein.

In the present invention, the source of the active auxiliary metal is not particularly limited, for example but not limited to at least one selected from the group consisting of active auxiliary metal chlorides, compounds of active auxiliary metal nitrates and compounds of active auxiliary metal acetates, etc.

A Pd-based bimetallic/polymetallic catalyst modified with an active auxiliary metal (for example, Cu) can improve the selectivity of isopropylbenzene of the catalyst, particularly in the initial stage. Preferably, the Pd content by weight

in the catalyst is greater than that of the active auxiliary metal (for example, Cu). That is, the ratio by weight of Pd to the active auxiliary metal (for example, Cu) is > 1 .

In a preferred embodiment, the content of the modifying auxiliary component (phosphorus and/or oxides thereof) in the catalyst is 0.2-20wt%. In a further preferred embodiment, the content of the modifying auxiliary component (phosphorus and/or oxides thereof) in the catalyst is 1-15wt%, more preferably 1-7wt%, wherein the content of phosphorus and/or oxides thereof is based on the content of element phosphorus therein.

The source of phosphorus in the present invention is not particularly limited, preferably but not limited to at least one selected from the group consisting of phosphoric acid, potassium dihydrogen phosphate, phosphorous acid and calcium phosphate.

Based on extensive experimental studies, the inventor found that the modification of the support with phosphorus could significantly improve the hydrogenation activity and stability of the catalyst, in particular hydrothermal stability. Particularly, the simultaneous introduction of an active auxiliary component (active auxiliary metal) in the catalyst had remarkable technical effects in respect of improving the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene.

In a preferred embodiment, if the support substrate is not silica, the modifying auxiliary component may further include silica.

In the catalyst of the present invention, the modification with silica (especially for modifying the support substrate of alumina) can improve the activity and stability of the catalyst. Preferably, alumina is used as the support substrate herein.

In a preferred embodiment (wherein the support substrate is not silica), the content of silica in the catalyst is >0 -60wt%, preferably >0 -40wt%, for

example, >0-20wt%, wherein the content of silica is based on the content of its molecules.

Here, the pore size of the catalyst increases after the modification with silicon, as improves the diffusion rate of the reactants and the product, thereby improving the conversion and the selectivity. In addition, it is also found that a silicon-containing catalyst has a better dehydration activity which is conducive to accelerate the rate of hydrogenolysis reaction.

In a preferred embodiment (wherein the support substrate is not silica), after the modification with silicon, the molar ratio of the silicon to phosphorus based on the element is ≤ 20 , preferably ≤ 10 , more preferably ≤ 4 , but not 0, wherein the content of the modifying auxiliary component of phosphorus and/or oxides thereof in the catalyst is 0.2-20wt%, preferably 1-15wt%, more preferably 1-7wt%, wherein the content of phosphorus and/or oxides thereof is based on the content of element phosphorus therein, and the silica content in the catalyst is >0-60wt%, preferably >0-40wt%, for example, >0-20wt%.

In this way, the high-temperature hydrothermal stability of the catalyst can be significantly improved. For example, the change of the specific surface area and the average pore size of the catalyst after the high-temperature hydrothermal treatment is significantly reduced. For example, preferably, the change of the specific surface area is less than 30% and the change of the average pore size is less than 20%; more preferably, the change of the specific surface area of the catalyst is less than 10% and the change of the average pore size is less than 10%.

Here, the temperature of the high-temperature hydrothermal treatment is 100-300°C and the period of the treatment is 20-300 hours.

The high-temperature hydrothermal stability is determined according to the following steps:

(a) Specific steps of high-temperature hydrothermal treatment of a catalyst: the catalyst is dispersed in excess water; then, the catalyst together with the water is placed in a crystallization kettle; after the crystallization kettle is sealed, it is placed in an oven of 200°C for 240 hours.

- 5 (b) A method for determining the specific surface area and the pore size of the catalyst comprises the following specific analysis steps: the physical properties of the catalyst support and the catalyst (such as the specific surface area, pore size, pore volume and the like) are analyzed by nitrogen physical adsorption (ASAP 2020M, Micromeritics). Before analysis and
10 tests, the sample is degassed in vacuum at 300°C for 3 hours to remove the adsorbed impurities and moisture in the sample. After that, the nitrogen adsorption-desorption isotherm of the test sample is analyzed under a liquid nitrogen environment (-196 °C).

The specific surface area (S_{BET}) of the sample is calculated based on the
15 nitrogen adsorption data under the relative pressure P/P_0 in the range of 0.05 - 0.20 according to BET equation (3-1):

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (3-1)$$

wherein P is the pressure practically measured; P_0 is the saturated vapor pressure at the adsorption temperature; V is the adsorption volume of
20 nitrogen under pressure P ; V_m is the volume of nitrogen required for monolayer saturated adsorption; C is the adsorption heat constant.

The pore size distribution (D_p) of the sample is calculated by BJH method (Barret-Joyner-Halensa) which is based on the phenomenon of capillary condensation. That is, the vapor pressure P and the radius of curvature of
25 the liquid r_k is in the following relationship:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2r \cdot V_m \cdot \cos\theta_k}{RT \cdot r_k} \quad (3-2)$$

wherein r is the surface tension of liquid nitrogen of 10^{-5} N/cm; V_m is the

molar volume of liquid nitrogen; θ_k is the contact angle between the meniscus and the solid hole wall; R is the ideal gas constant; T is the test temperature. Adsorption capacity V under different pressure P/P_0 was obtained in the experiments. The relationship between V and r_k is obtained
5 by formula (3-2). Plotting of r_k with dV/dr_k results in the curve of the pore size distribution of the sample.

In a preferred embodiment, the catalyst further includes a co-catalyst; more preferably, the co-catalyst is a sulfur-containing compound which is preferably derived from a sulfur-containing organic matter.

10 Preferably, the support and the active component supported thereon are the catalyst main body on which the co-catalyst is supported.

In a further preferred embodiment, the content of the co-catalyst in the catalyst is $>0.1\text{wt}\%$, preferably $>0.8\text{wt}\%$, wherein the amount of the co-catalyst is based on the amount of effective elements therein, for
15 example, the amount of element sulfur.

In the present invention, the source of the sulfur-containing compound is not particularly limited, preferably but not limited to at least one selected from the group of tert-nonyl polysulfides, tert-butyl polysulfides, thiophenes and dimethyl disulfides etc..

20 The sulfur-containing compound is preferentially adsorbed on the low coordination unsaturated active center on the catalyst surface, which causes the local poisoning phenomenon of an unstable active center on the catalyst. In this way, it can better inhibit the local overheating of the catalyst caused by a relatively high initial activity of the catalyst, and avoid
25 the growth of metal grains and the excessive hydrogenation of isopropylbenzene to isopropylcyclohexane. Meanwhile, it can effectively control the generation of dimerized isopropyl benzene (2,3-dimethyl-2,3-diphenylbutane), significantly improving the operation stability of the catalyst while enhancing the selectivity of isopropylbenzene.

The metal palladium on the catalyst is free of a compressed double-bridge-bonded CO adsorption site. Preferably, there is no absorption peak in the range of 2000-1950cm⁻¹ in the *in situ* infrared spectrogram of carbon monoxide adsorption of the catalyst.

- 5 In a preferred embodiment, the metal palladium on the catalyst contains a linear-bonded CO adsorption site, a mono-bridge-bonded CO adsorption site and a face-bonded CO adsorption site. In a further preferred embodiment, there are absorption peaks in the ranges of 2150-2050 cm⁻¹, 1950-1900 cm⁻¹ and 1900-1850 cm⁻¹ in the *in situ* infrared spectrogram of
10 carbon monoxide adsorption of the catalyst.

In general, a metal palladium catalyst has four CO adsorption sites of special characteristics which respectively correspond to the noticeable absorption peaks in ranges of 2150-2050cm⁻¹, 2000-1950cm⁻¹, 1950-1900cm⁻¹ and 1900-1850 cm⁻¹ in the CO-FTIR spectrogram. Said
15 absorption peaks respectively belong to the linear-bonded CO adsorption site, compressed double-bridge-bonded CO adsorption site, mono-bridge-bonded CO adsorption site and face-bonded CO adsorption site of CO on the Pd surface.

The infrared spectrogram of CO adsorbed on the catalyst surface is
20 determined as follows:

CO Fourier Transform Infrared spectrogram (CO-FTIR): FT-IR test of CO adsorption is carried out on an infrared spectrometer of THERMO NICOLET 4700 NEXUS with a resolution of 4cm⁻¹. A sample is subjected to a pre-treatment of reduction in a Harrick *in situ* pool. The background
25 spectrogram is first scanned at the test temperature before introducing CO gas for adsorption. Upon adsorption equilibrium, the sample is purged with nitrogen until no gas-phase infrared absorption peak of CO can be detected. The infrared spectrogram at the determination temperature is collected and the background spectrogram at the corresponding temperature is subtracted
30 to obtain the infrared spectrogram of CO adsorbed on the catalyst surface.

The second object of the present invention is to provide a method for producing the catalyst according to the first object of the present invention, comprising the following steps:

Step 1: an aqueous solution of a phosphorus-containing compound is
5 mixed with a support substrate, dried and calcined to obtain a phosphorus-containing support;

Step 2: the support is added to a solution of a palladium-containing compound, dried and calcined to obtain a catalyst precursor in an oxidized state;

10 Step 3: the catalyst precursor in an oxidized state is subjected to a reduction treatment to obtain a catalyst.

In a preferred embodiment, step 1' is optionally performed after step 1 and before step 2:

Step 1': the phosphorus-containing support is mixed with an aqueous
15 solution of silica gel, dried and calcined to obtain a support containing phosphorus and silicon.

In a preferred embodiment, in step 1, step 2 and step 1', the drying is carried out by drying at 60-200°C for 4-36 hours, preferably at 150°C for 6 hours, or preferably at 110°C for 8 hours.

20 In a preferred embodiment, in step 1, step 2 and step 1', the calcining temperature is 400-700°C, preferably 400-500°C.

In the present invention, the phosphorus-containing compound in step 1 is not particularly limited, preferably but not limited to at least one selected from the group consisting of phosphoric acid, potassium dihydrogen
25 phosphate, phosphorous acid, calcium phosphate and ammonium hydrogen phosphate, etc.

In a preferred embodiment, the solution of a palladium-containing

compound in step 2 further comprises a compound containing an active auxiliary metal.

In the present invention, unless otherwise specified, the support substrate is not particularly limited, preferably at least one selected from the group consisting of alumina, silica and activated carbon, more preferably alumina; the palladium-containing compound is not particularly limited, preferably but not limited to at least one selected from the group consisting of palladium chloride, palladium nitrate and chloropalladic acid; the compound containing an active auxiliary metal is not particularly limited, for example but not limited to at least one selected from the group consisting of active auxiliary metal chlorides, compounds of active auxiliary metal nitrates and compounds of active auxiliary metal acetates and the like; preferably, the active auxiliary metal is at least one selected from the group consisting of metal copper, metal zinc, metal cobalt, metal tin, metal nickel and metal silver, for example, metal copper.

In a preferred embodiment, in step 3, the reduction treatment is carried out with hydrogen. In a further preferred embodiment, the reduction temperature in step 3 is 40-300°C, preferably 200-300°C, more preferably 250°C; the volume space velocity of hydrogen is 50-500h⁻¹, preferably 80-150h⁻¹, more preferably 100h⁻¹.

In a preferred embodiment, the method further comprises step 4:

Step 4: the catalyst according to step 3 is added to a co-catalyst-containing solution and dried to obtain a further catalyst.

In a further preferred embodiment, the co-catalyst is a sulfur-containing compound; more preferably, the sulfur-containing compound is derived from a sulfur-containing organic matter; further preferably, the sulfur-containing organic matter is at least one selected from the group of tert-nonyl polysulfides, tert-butyl polysulfides, thiophenes and dimethyl disulfides.

In the production method according to the present invention, the amounts of the palladium-containing compound and the phosphorus-containing compound based on 1L of the support substrate are as follows:

the amount of the palladium-containing compound is preferably
5 0.06g/L-30g/L, more preferably 0.5g/L-10g/L, based on the amount of element palladium therein, and;

the amount of the phosphorus-containing compound is preferably 2g/L-100g/L, more preferably 5g/L-80g/L, based on the amount of element phosphorus therein.

10 If present, the amounts of the compound containing an active auxiliary metal, the silica gel and/or the sulfur-containing organic matter are based on 1L of the support substrate as follows:

the amount of the compound containing an active auxiliary metal is preferably 0.0006g/L-1.2g/L, more preferably 0.01g/L-1.0g/L, based on
15 the amount of the element of the active auxiliary metal therein;

the amount of silica gel is 6-300g/L, more preferably 20-200g/L, wherein the amount of silica gel is based on the amount of silica therein;

the amount of the co-catalyst, e.g., a sulfur-containing compound, is 0.0001g/L-3g/L, preferably 0.01g/L-1g/L, more preferably 0.05g/L-0.2 g/L,
20 wherein the amount of the sulfur-containing compound is based on the amount of effective elements therein, such as element sulfur.

In the method for producing a catalyst of the present invention, all solutions are those formed by fully dissolving solutes in their good solvents, preferably aqueous solutions.

25 The third object of the present invention is to provide the use of the catalyst according to the first object of the present invention or the catalyst obtained by the method according to the second object of the present

invention in the production of isopropylbenzene.

The fourth object of the present invention is to provide a method for producing isopropylbenzene, in particular, a method for producing isopropylbenzene from α,α -dimethylbenzyl alcohol, preferably carried out
5 with the catalyst according to the first object of the present invention or the catalyst obtained by the method according to the second object of the present invention.

In a preferred embodiment, the production method comprises: bring the raw material in contact with hydrogen to react in the presence of the
10 catalyst to obtain isopropylbenzene. In a further preferred embodiment, the raw material comprise a hydrocarbon material comprising α,α -dimethylbenzyl alcohol. In a further preferred embodiment, the hydrocarbon material comprising α,α -dimethylbenzyl alcohol comprises an inert solvent (preferably isopropylbenzene) and α,α -dimethylbenzyl alcohol.
15 For example, the hydrocarbon material is the column bottom liquid after propylene oxide is separated in the production of propylene oxide in the isopropylbenzene hydroperoxide process, and/or the material obtained from the reduction of isopropylbenzene hydroperoxide. Here, the inert solvent must be substantively inactive to the reactants and the resultants,
20 for example, long-chain alkanes (octane, dodecane) and aromatic monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, n-propyl benzene, n-butyl benzene, isopropylbenzene), etc. Specifically, the inert solvent is a hydrocarbon substantively inactive to the reactants and the resultants. Moreover, the solvent can be an organic solvent having a
25 good compatibility with dimethylbenzyl alcohol, but preferably isopropylbenzene which does not affect the subsequent reaction.

In a preferred embodiment, the raw material comprises 1-100% of α,α -dimethylbenzyl alcohol and 0-99% of an inert solvent (preferably isopropylbenzene). In a further preferred embodiment, the raw material
30 comprises 50-75% of α,α -dimethylbenzyl alcohol and 25-50% of an inert

solvent (preferably isopropylbenzene).

In the present invention, the specific content of each component in the raw material is not particularly limited. As a non-restrictive example, the raw material comprise about 55wt% of a hydrocarbon material of α,α -dimethylbenzyl alcohol, about 43wt% of isopropylbenzene and other hydrocarbons in content of about 2wt%, based on the weight percentage. The other hydrocarbons may include n-propyl benzene, methylstyrene, acetophenone and 2,3-dimethyl-2,3-diphenylbutane.

In a preferred embodiment, the pressure is 0.1-4.0MPa, the temperature is 130-220°C, the liquid hourly space velocity is 1-20 h⁻¹, and the molar ratio of hydrogen to α,α -dimethylbenzyl alcohol is > 4 in the production method. In a further preferred embodiment, the pressure is 0.5-3.0MPa, the temperature is 150-200°C, the liquid hourly space velocity is 4-15 h⁻¹, and the molar ratio of hydrogen to α,α -dimethylbenzyl alcohol is > 5.

In a preferred embodiment, the production method employs the liquid phase thermal cycle process. Preferably, the cycle ratio is 1-10, preferably 4-8. The "liquid phase thermal cycle process" herein refers to a direct circulation of the liquid phase thermal material at the outlet of a catalyst bed to the catalyst bed without cooling and water separation.

In a preferred embodiment, the production method of the present invention comprises obtaining the isopropylbenzene from raw material of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol and hydrogen through a first catalyst bed and a second catalyst bed in series, preferably by the liquid phase thermal cycle process;

wherein,

the catalyst loading of the first catalyst bed is greater than or equal to that of the second catalyst bed;

the inlet temperature of the first catalyst bed is not higher than the inlet

temperature of the second catalyst bed;

the liquid phase thermal cycle ratio of the first catalyst bed is preferably 1-10;

the liquid phase thermal cycle ratio of the second catalyst bed is preferably
5 0-2.

In a preferred embodiment, the ratio by volume of the catalyst loading of the first catalyst bed to the catalyst loading of the second catalyst bed is (1-6): 1, preferably (2-4): 1.

In the first catalyst bed, the ratio by volume of hydrogen to the liquid phase
10 is preferably 300-1000, more preferably 400-800, and/or; in the second catalyst bed, the ratio by volume of hydrogen to the liquid phase is preferably 100-800, more preferably 200-400.

In a preferred embodiment, the first catalyst bed has a reaction temperature of 130-190°C, a reaction pressure of 0.1-5MPa, and a liquid hourly space
15 velocity of 1.0-20h⁻¹. In a further preferred embodiment, the first catalyst bed has a reaction temperature of 150-170°C, a reaction pressure of 0.5-3.0MPa, a liquid phase volume space velocity of 1-5h⁻¹, and a cycle ratio of 2-8.

Here, the liquid phase is a fresh oil which refers to a raw material feed that
20 has not undergone a dilution by the liquid phase thermal cycle process. In a preferred embodiment, the second catalyst bed has a reaction temperature of 150-230°C, a reaction pressure of 0.1-5 MPa, and a liquid phase volume space velocity of 2.0-10h⁻¹. In a further preferred embodiment, the second catalyst bed has a reaction temperature of 160-190°C, a reaction pressure
25 of 0.5-3MPa, and a liquid hourly space velocity of 4-8 h⁻¹.

Preferably, the catalyst of the first catalyst bed comprises metal Pd and/or oxides, and a support.

Preferably, the catalyst of the second catalyst bed comprises metal Pd and/or oxides, a metal auxiliary and/or oxides thereof, and a support; preferably, the metal auxiliary is at least one selected from the group consisting of Fe, Co, Ni, Ca, Mg and Cu, more preferably at least one
5 selected from the group consisting of Cu, Ni and Mg.

Preferably, the catalyst of the first catalyst bed and/or the catalyst of the second catalyst bed are the catalysts for producing isopropylbenzene as provided in the first object of the present invention.

In the present invention, the loading of the first catalyst bed is set to be
10 greater than or equal to, preferably significantly higher than the loading of the second catalyst bed, so that the raw material can react in the first catalyst bed as much as possible. If there is unreacted raw material, it enters the second catalyst bed for a reaction at a slightly higher temperature. Specifically, when the concentration of reactants in the raw material is
15 high, the heat release in the reaction process is high, so the first bed adopts the mode of the liquid phase thermal cycle, having a high total volume space velocity and a function of carrying heat to prevent an overheating of the bed and a formation of local hot spots, as is conducive to the selectivity and stability of the catalyst. Whereas, the second bed which employs a
20 higher temperature realizes a high conversion of a small amount of remained reactants. In this way, the impurity content in the product is significantly reduced.

In a preferred embodiment, the conversion of α,α -dimethylbenzyl alcohol is greater than 99.5% and the selectivity of isopropylbenzene is greater than
25 99.8% in the method for producing isopropylbenzene from α,α -dimethylbenzyl alcohol.

The conversion and the selectivity are calculated according to the following formula:

α,α -dimethylbenzyl alcohol conversion (%) = $[(W^0_1 - W^t_1) / W^0_1] \times 100\%$;

Isopropylbenzene selectivity (%)=[((W^t₂- W⁰₂)/M₂)/((W⁰₁-W^t₁)/M₁)]×100% ;

wherein, w⁰₁ denotes the mass of α,α-dimethylbenzyl alcohol in the raw material; w^t₁ denotes the mass of α,α-dimethylbenzyl alcohol in the product; w⁰₂ notes the mass of isopropylbenzene in the raw material; w^t₂ denotes the mass of isopropylbenzene in the product; M₁ denotes the molecular weight of α,α-dimethylbenzyl alcohol; M₂ denotes the molecular weight of isopropylbenzene.

The method for producing isopropylbenzene from α,α-dimethylbenzyl alcohol according to the present invention provides a suitable dehydrating acid site and a hydrogenating metal active site, better inhibits the local overheating of the catalyst caused by a relatively high initial activity of the catalyst, avoids the growth of metal grains and the excessive hydrogenation of isopropylbenzene to isopropylcyclohexane in the catalytic process of producing isopropylbenzene by dehydration and hydrogenation of α,α-dimethylbenzyl alcohol in the presence of a supported palladium active component. Meanwhile, it effectively controls the generation of dimerized isopropyl benzene and significantly improves the operation stability of the catalyst while enhancing the selectivity of isopropylbenzene.

The present invention further provides the use of the said production method in the production of propylene oxide, for example by:

Step 1: obtaining isopropylbenzene hydroperoxide by oxidation of isopropylbenzene;

Step 2: obtaining propylene oxide and α,α-dimethylbenzyl alcohol from the reaction of isopropylbenzene hydroperoxide and propylene;

Step 3: obtaining a hydrocarbon material comprising α,α-dimethylbenzyl alcohol by means of a separation of propylene oxide by rectification;

Step 4: subjecting the hydrocarbon material comprising α,α-dimethylbenzyl alcohol to a treatment with the catalyst and the method

in the present invention to obtain isopropylbenzene which is recycled to step 1 for reuse.

The endpoints and any values of the ranges disclosed in the present invention are not limited to the precise ranges or values. These ranges or values should be interpreted as including the values close to these ranges or these values. In regard of number ranges, between the endpoints of each range, between the endpoints of each range and the individual values, and between the individual values, they can be combined with each other to obtain one or more new number ranges. It should be regarded that these number ranges are specifically disclosed in the present invention. Various technical solutions in the context can be combined with each other in principle to obtain new technical solutions, which should also be regarded as being specifically disclosed in the present invention.

The present invention at least has the following advantageous effects compared with the prior art:

(1) the addition of a modifying auxiliary component P in the support of the catalyst according to the present invention can significantly improve and increase the hydrogenation activity and the stability of the catalyst. In particular, the addition of the modifying auxiliary components P and SiO₂ in the support can significantly improve the hydrothermal stability of the catalyst when the molar ratio of silicon to phosphorus is of a certain value.

(2) the simultaneous introduction of the active auxiliary component in the catalyst can significantly improve the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene.

(3) the introduction of a co-catalyst in the catalyst avoids the excessive hydrogenation of isopropylbenzene to isopropylcyclohexane. Meanwhile, it can effectively control the generation of dimerized isopropyl benzene (2,3-dimethyl-2,3-diphenylbutane), and significantly improve the operation stability of the catalyst while enhancing the selectivity of isopropylbenzene.

(4) in the method for producing isopropylbenzene by the liquid phase thermal cycle provided in the present invention, the utilization of the reaction heat is more reasonable, as can significantly reduce the energy consumption and costs of the device and produce isopropylbenzene efficiently.

(5) the method for producing isopropylbenzene according to the present invention provides a suitable dehydrating acid site and hydrogenating metal active site, better inhibits the excessive hydrogenation of isopropylbenzene to isopropylcyclohexane due to the local overheating of the catalyst caused by a relatively high initial activity of the catalyst in the catalytic process of producing isopropylbenzene by dehydration and hydrogenation of α,α -dimethylbenzyl alcohol in the presence of a supported palladium active catalyst. Meanwhile, it effectively controls the generation of dimerized isopropyl benzene and significantly improves the operation stability of the catalyst while enhancing the selectivity of isopropylbenzene.

In conclusion, the present invention produces a hydrogenolysis catalyst having good properties, realizes the coupling of two reactions of dehydration and hydrogenation and utilizes energy more reasonably by using the liquid phase thermal cycle process by means of producing a support having a good hydrothermal stability and an excellent dehydration property and supporting hydrogenating metals using the support. Meanwhile, the present invention prevents the decrease in the performance of the catalyst caused by the local overheating of the catalyst bed and realizes a low-cost and highly-efficient production of isopropylbenzene.

Mode for Carrying out the Invention.

The present invention is described in detail in combination with specific examples as below. It is necessary to point out that the following examples which are only used for further illustration of the present invention cannot be interpreted as a limitation on the protection scope of the present

invention. Non-essential improvements and adjustments made by those skilled in the art to the present invention according to the contents of the present invention are still in the protection scope of the invention.

Table 1 shows the components of the raw material used in the examples
5 and the comparative examples.

Table 1 : Components of the used raw material

Components of raw material	Components by weight w%
isopropylbenzene	43.25
n-propyl benzene	0.08
methylstyrene	0.12
acetophenone	1.02
α,α -dimethylbenzyl alcohol	55.26
dimerized isopropylbenzene (2,3-dimethyl-2,3-diphenylbutane)	0.27

Analysis of the content of each component in the catalyst: the specific
10 element composition in the catalyst is determined by X-ray fluorescence analysis method. Different elements have characteristic X-ray spectrogram with different wavelengths, and the fluorescence intensity of each spectral line has a certain relationship with the concentration of the element. Qualitative and quantitative analysis can be performed by determining the
15 wavelength and intensity of the characteristic X-ray spectral lines of the elements to be tested.

I. Production and evaluation of catalysts

Example 1

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

- 5 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having
10 a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

- 15 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

- 20 Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

- 25 The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 2

1. Catalyst production

- 5 1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of
10 copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based
15 catalyst.

The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was
20 filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

25 Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h^{-1}

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

5 Example 3

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400°C for 4 hours to produce a catalyst support.

- 10 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 15 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour^{-1} for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

The major components and properties of the catalyst are shown in Table 2 and Table 3. The CO-FTIR analysis results are shown in Fig.1.

20 2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

- 25 The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

5 Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 4

10 1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 35g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

15 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

20 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

- 5 The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

- 10 Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 5

- 15 1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 5.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

- 20 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 25 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based

catalyst.

The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

- 5 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

- 10 Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

- 15 The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 6

1. Catalyst production

- 20 1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of

copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst precursor II.

1L of the above palladium-based catalyst precursor II was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur and dried at 110°C to obtain a palladium-based catalyst.

10 The major components and properties of the catalyst are shown in Table 2 and Table 3. The CO-FTIR analysis results are shown in Fig.1.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

20 Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 7

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 35g of P, dried at 110°C for 8 hours and calcined at 400 °C for 5 4 hours to produce a catalyst support.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

10 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst precursor II.

15 1L of the above palladium-based catalyst precursor II was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur and dried at 110°C to obtain a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

20 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

25 Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h^{-1}

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 1000 hour evaluation are shown in Table 5.

5 Example 8

The process in Example 2 was repeated, except that the aqueous solution of chloropalladic acid-nickel nitrate contained 10.0g of palladium and 1.2g of nickel. The major components of the catalyst are shown in Table 2.

The catalyst evaluation in Example 2 was repeated. Likewise, the
10 conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were both relatively high.

Example 9

The process in Example 2 was repeated, except that the aqueous solution of chloropalladic acid-cobalt nitrate contained 0.5g of palladium and 0.0006g
15 of cobalt. The major components of the catalyst are shown in Table 2.

The catalyst evaluation in Example 2 was repeated. Likewise, the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were both relatively high.

Examples 10-13

20 The process in Example 7 was repeated, except that di-tertnonyl polysulfides containing 0.01g, 0.05g, 0.2g and 1g of sulphur were respectively employed. The major components of the catalyst are shown in Table 2.

The catalyst evaluation in Example 7 was repeated. Likewise, the
25 conversion of α,α -dimethylbenzyl alcohol and the selectivity of

isopropylbenzene were both relatively high.

Example 14

The process in Example 6 was repeated, except that in the catalyst production:

- 5 1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 5% of SiO₂,
10 dried and calcined at 500°C to obtain a support containing P/Si.

1L of the above support containing P/Si was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 15 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst precursor II.

1L of the above palladium-based catalyst precursor II was impregnated
20 with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2.

The catalyst evaluation in Example 6 was repeated. Likewise, the conversion of α,α -dimethylbenzyl alcohol and the selectivity of
25 isopropylbenzene were both relatively high.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 15

The process in Example 6 was repeated, except that in the catalyst production:

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO₂, dried and calcined at 500°C to obtain a support containing P/Si.

10 1L of the above support containing P/Si was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst precursor II.

1L of the above palladium-based catalyst precursor II was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2.

The support employed in the catalyst obtained in Example 15 contained not only P but also silicon. In the production of isopropylbenzene by hydrogenation of α,α -dimethylbenzyl alcohol using the catalyst, the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were both higher than those in Example 6.

The physical properties of the catalyst after high-temperature hydrothermal

treatment are shown in Table 4.

Example 16

The process in Example 6 was repeated, except that in the catalyst production:

- 5 1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 20% of SiO₂,
10 dried and calcined at 500°C to obtain a support containing P/Si.

1L of the above support containing P/Si was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 15 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst precursor II.

1L of the above palladium-based catalyst precursor II was impregnated
20 with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

25 Example 17

The process in Example 6 was repeated, except that in the catalyst

production:

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

- 5 1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 30% of SiO₂, dried and calcined at 500°C to obtain a support containing P/Si.

- 1L of the above support containing P/Si was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium
10 and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500 °C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based
15 catalyst precursor II.

1L of the above palladium-based catalyst precursor II was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2.

- 20 The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

- Analysis of Examples 14-17: the supports employed in the catalysts obtained in Examples 14-17 contained not only P, but also silicon and sulfur. When the above were used in the production of isopropylbenzene by
25 hydrogenation of α,α -dimethylbenzyl alcohol, both the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were higher than those in Example 6.

Example 18

The process of Example 14 was repeated, except that in the catalyst evaluation:

Hydrogenation operation was carried out in a fixed bed reactor which was
5 filled with the catalyst produced as the above. Hydrogenation operation of
a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried
out in a continuous manner. The material first passed through the first
catalyst bed, and then through the second catalyst bed. The catalyst loading
volume ratio of the two catalyst beds was 4:1. The operating conditions of
10 the two reactors were as follows:

The first catalyst bed:

Inlet temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 2.0 h⁻¹

15 Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The second catalyst bed:

Inlet temperature: 160°C

Reaction pressure: 2.0MPa

20 Liquid phase thermal cycle ratio: 0

The average results of 200 hour evaluation are shown in Table 5.

Example 19

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO₂, dried and calcined at 500°C to obtain a support containing P/Si.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Example 20

1. Catalyst production

- 5 1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours
10 and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based
15 catalyst.

1L of the above palladium-based catalyst precursor was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2.

20 2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

- 25 The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h^{-1}

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

- 5 The average results of 200 hour evaluation are shown in Table 5.

Example 21

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid
10 containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400°C for 4 hours to produce a catalyst support.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO_2 , dried and calcined at 500°C to obtain a support containing P/Si.

15 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was
20 reduced with hydrogen having a volume space velocity of 100 hour^{-1} for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

1L of the above palladium-based catalyst precursor was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of
25 sulphur to obtain a palladium-based catalyst. The major components and

properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of
5 a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

10 Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal
15 treatment are shown in Table 4.

Example 22

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 8.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for
20 4 hours to produce a catalyst support.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO₂, dried and calcined at 500°C to obtain a support containing P/Si.

1L of the above support was mixed with 2000g of aqueous solution of

chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500 °C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

5 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2.

2. Catalyst evaluation

10 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

15 Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

20 Example 23

1. Catalyst production

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid containing 4.0g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO₂, dried and calcined at 500°C to obtain a support containing P/Si.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal

treatment are shown in Table 4.

Comparative Example 1

1. Catalyst production

1L of alumina was mixed with 2000g of aqueous solution of chloropalladic
5 acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined
at 500°C for 4 hours to produce a palladium-based catalyst precursor I in
an oxidized state. The above palladium-based catalyst precursor I in an
oxidized state was reduced with hydrogen having a volume space velocity
of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a
10 palladium-based catalyst.

The major components and properties of the catalyst are shown in Table 2
and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was
15 filled with the catalyst produced as the above. Hydrogenation operation of
a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried
out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

20 Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Comparative Example 2

1. Catalyst production

- 5 1L of alumina was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500 °C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with
10 hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

- 15 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

- 20 Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

- 25 The average results of 200 hour evaluation are shown in Table 5.

Comparative Example 3

1. Catalyst production

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

1L of the above palladium-based catalyst was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

Comparative Example 4

5 1. Catalyst production

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 10 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

- 15 1L of the above palladium-based catalyst was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

- 20 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

- 25 Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h^{-1}

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

5 Comparative Example 5

1. Catalyst production

1L of support alumina was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO_2 , dried and calcined at 500°C to obtain a support containing Si.

- 10 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

- 15 The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour^{-1} for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst. The major components and properties of the catalyst are shown in Table 2.

- 20 The major components and properties of the catalyst are shown in Table 2 and Table 3.

2. Catalyst evaluation

- 25 Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

5 Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

The physical properties of the catalyst after high-temperature hydrothermal treatment are shown in Table 4.

10 Comparative Example 6

1. Catalyst production

1L of support alumina was mixed with 600g of aqueous solution of silica gel having a mass concentration of 10% of SiO₂, dried and calcined at 500°C to obtain a support containing Si.

15 1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state.

The above palladium-based catalyst precursor I in an oxidized state was
20 reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 250°C to produce a palladium-based catalyst.

1L of the above palladium-based catalyst was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur
25 to obtain a palladium-based catalyst. The major components of the catalyst

are shown in Table 2.

The major components and properties of the catalyst are shown in Table 2.

2. Catalyst evaluation

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalyst produced as the above. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

10 Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 200 hour evaluation are shown in Table 5.

15

Table 2 : Major components of the catalysts

Item	Al ₂ O ₃ wt%	Pd wt%	M wt%	P wt%	S wt%	SiO ₂ wt%
Example 1	95.24	0.458	0	1.39	0	0
Example 2	95.24	0.458	CuO-0.19	1.41	0	0
Example 3	87.55	0.467	CuO-0.18	4.6	0	0
Example 4	84.45	0.466	CuO-0.19	6.12	0	0
Example 5	97.11	0.482	CuO-0.19	0.89	0	0
Example 6	87.47	0.457	CuO-0.18	4.7	0.020	0
Example 7	84.36	0.463	CuO-0.19	6.27	0.021	0

Example 8	94.32	1.527	NiO-0.26	1.41	0	0
Example 9	95.24	0.078	CoO-0.00014	1.39	0	0
Example 10	84.22	0.456	CuO-0.226	6.28	0.0019	0
Example 11	83.61	0.462	CuO-0.225	6.31	0.010	0
Example 12	83.58	0.459	CuO-0.227	6.29	0.036	0
Example 13	82.90	0.467	CuO-0.223	6.33	0.200	0
Example 14	81.86	0.452	CuO-0.228	4.75	0.020	5.45
Example 15	76.98	0.423	CuO-0.226	4.67	0.021	10.62
Example 16	64.25	0.478	CuO-0.226	4.91	0.019	21.26
Example 17	53.56	0.465	CuO-0.224	4.76	0.020	33.05
Example 19	85.32	0.458	0	1.39	0	10.62
Example 20	95.86	0.458	0	1.39	0.021	0
Example 21	85.25	0.458	0	1.39	0.021	10.62
Example 22	85.11	0.458	CuO-0.19	1.39	0	10.62
Example 23	86.72	0.458	CuO-0.19	0.72	0	10.62
Comparative Example 1	99.21	0.471	0	0	0	0
Comparative Example 2	99.17	0.467	CuO-0.228	0	0	0
Comparative Example 3	99.17	0.467	CuO-0.19	0	0.021	0
Comparative Example 4	99.36	0.467	0	0	0.021	0
Comparative Example 5	88.66	0.467	0	0	0	10.62
Comparative Example 6	88.61	0.467	0	0	0.021	10.62

Table 3 : Physical properties of the obtained catalysts

Item	Specific surface area	Average pore size	Pd dispersity
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	m ² /g	nm	%
Example 1	138	13.5	9.6
Example 2	138	13.7	8.5
Example 3	133	14.8	6.9
Example 4	128	14.7	6.5
Example 5	142	13.2	8.4
Example 6	133	14.8	6.9
Example 7	128	15.2	6.5
Example 8	135	13.5	5.2
Example 11	127	14.6	7.2
Example 14	132	13.8	6.9
Example 15	141	13.6	6.5
Example 16	145	12.9	6.7
Example 17	151	13.1	6.6
Example 19	136	13.4	9.8
Example 21	136	13.4	8.2
Example 23	141	13.2	8.5
Comparative Example 1	146	12.7	21.3
Comparative Example 2	146	12.7	18.3
Comparative Example 3	146	12.7	15.4
Comparative Example 4	146	12.7	12.3
Comparative Example 5	154	11.9	13.6

Table 4: Physical properties of the produced catalysts after high-temperature hydrothermal treatment

Item	Specific surface area (m ² /g)	Average pore size (nm)
Example 1	102	16.2
Example 3	108	15.8

Example 4	116	14.6
Example 5	102	16.4
Example 6	112	15.4
Example 14	142	13.2
Example 15	146	12.8
Example 16	152	12.6
Example 17	156	12.8
Example 19	152	12.8
Example 21	155	12.6
Example 23	128	13.8
Comparative Example 1	32	24.2
Comparative Example 3	35	23.6
Comparative Example 5	86	17.6

Table 4 proves that the physical properties of the catalysts of Examples 1, 3-6, 14-17, 19, 21 and 23 of the present invention after high-temperature hydrothermal treatment are excellent.

Table 5: Average results of 200 hour evaluation

Item	Production quantity of isopropylcyclohexane ppm	Conversion of α,α -dimethylbenzyl alcohol %	Selectivity of isopropylbenzene %
Example 1	556	99.22	99.75
Example 2	418	99.54	99.81
Example 3	321	99.42	99.84
Example 4	412	99.41	99.78
Example 5	376	99.51	99.77
Example 6	139	99.71	99.88
Example 7	128	99.66	99.87
Example 8	524	99.71	99.68
Example 9	278	99.58	99.82
Example 10	238	99.74	99.78
Example 11	185	99.81	99.81
Example 12	89	99.65	99.92
Example 13	45	99.52	99.88
Example 14	16	99.75	99.90
Example 15	14	99.75	99.87
Example 16	12	99.70	99.86
Example 17	15	99.70	99.86
Example 18	6	99.95	99.90
Example 19	456	99.36	99.78
Example 20	145	99.46	99.82
Example 21	125	99.58	99.85
Example 22	325	99.51	99.80
Example 23	336	99.42	99.78
Comparative Example 1	920	97.45	99.45
Comparative Example 2	721	97.32	99.58

Comparative Example 3	386	97.62	99.68
Comparative Example 4	425	97.56	99.62
Comparative Example 5	856	98.24	99.68
Comparative Example 6	125	98.56	99.72

At least the followings can be seen from Table 2, Table 3, Table 4, Table 5 and Fig.1:

- (1) according to the comparison of Example 1 and Comparative Example 1,
5 the hydrothermal stability of the support was significantly improved and the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were significantly improved after adding phosphorus to the support;
- (2) according to the comparison of Example 1 and Example 2, when a
10 Pd-Cu composite active component was used, both the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were higher than those of a mere Pd active component;
- (3) according to the comparison of Example 1 and Example 19, the
hydrothermal stability of the support was further improved, and the
15 conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were further improved after introducing silica to the support;
- (4) according to the comparison of Example 1 and Example 20, the
conversion of α,α -dimethylbenzyl alcohol and the selectivity of
20 isopropylbenzene were further improved after introducing sulfur to the catalyst;

(5) according to the comparison of Example 3 and Example 6, there was no compressed double-bridge-bonded CO adsorption site on CO-FTIR spectrogram (see Fig.1); the production quantity of isopropylcyclohexane was significantly reduced, and the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were significantly improved after adding S to the catalyst;

(6) according to the respective comparison of Examples 14-17 and Examples 1-13, the production quantity of isopropylcyclohexane was significantly reduced when introducing Cu, S and Si to the catalyst simultaneously.

(7) according to comparison of Example 18 and Example 14, the conversion of α,α -dimethylbenzyl alcohol and the selectivity of isopropylbenzene were significantly improved when a reaction process of two stages of catalyst beds in series was used in relative to the use of one stage of catalyst bed.

(8) all the catalysts in Comparative Examples 3-6 were free of phosphorus, and the conversion of α,α -dimethylbenzyl alcohol was inferior and the selectivity of isopropylbenzene was relatively low.

Stability test of one thousand hours:

Hydrogenation operation was carried out in a fixed bed reactor which was filled with the catalysts produced in Example 14 and Comparative Example 1 respectively. Hydrogenation operation of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol was carried out in a continuous manner.

The operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 2.0MPa

Volume space velocity of raw material fresh oil: 1.6h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ α,α -dimethylbenzyl alcohol molar ratio: 8

The average results of 1000 hour evaluation are shown in Table 6.

5 Table 6: Average results of 1000 hour evaluation

Item	Time hours	Production quantity of isopropylcyclohexane ppm	Conversion of α,α -dimethylbenzyl alcohol %	Selectivity of isopropylbenzene %
Catalyst produced in Example 14	200	16	99.75	99.90
	400	15	99.76	99.89
	600	6	99.72	99.88
	800	6	99.78	99.88
	1000	0	99.79	99.90
Catalyst produced in Comparative Example 1	200	920	97.32	99.45
	400	854	97.28	99.56
	600	556	97.12	99.61
	800	376	96.68	99.71
	1000	236	96.44	99.78

Stability test of one thousand hours was carried out on the catalysts prepared in Example 14 and Comparative Example 1 respectively. It can be
10 learnt from Table 6 that the catalyst of the present invention not only significantly reduced the production quantity of isopropylcyclohexane in the stage of the initial activity of the catalyst but also remained stable for one thousand hours with the conversion of α,α -dimethylbenzyl alcohol $\geq$ 99.72% and the selectivity of isopropylbenzene $\geq$ 99.88% in the evaluation
15 of the 1000 hour reaction, as indicated that performance of the catalyst did not undergo a significant change.

II. A method for producing isopropylbenzene from α,α -dimethylbenzyl alcohol

The method for producing isopropylbenzene from α,α -dimethylbenzyl alcohol of the present invention results in the isopropylbenzene from raw material of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol and hydrogen through a first catalyst bed and a second catalyst bed in series, preferably by the liquid phase thermal cycle process. Relevant examples and comparative examples are listed as below, which however cannot be interpreted as a limitation of the present invention.

10 [Example 1']

1. Catalyst production

a. Production of the catalyst of the first catalyst bed

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 450°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

b. Production of the catalyst of second catalyst bed

1L of the support alumina was mixed with 2000g of aqueous solution of chloropalladic acid-nickel nitrate containing 3.0g of palladium and 0.3g of nickel, dried at 110°C for 8 hours and calcined at 550°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based

catalyst. The specific components of the catalyst are shown in Table 2'.

2. Catalyst evaluation

Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous
5 manner. The material first passed through the first catalyst bed, and then through the second catalyst bed. The catalyst loading volume ratio of the two catalyst beds was 4:1. The operating conditions of the two reactors were as follows:

The first catalyst bed:

10 Reaction temperature: 150°C

Reaction pressure: 1.5MPa

Volume space velocity of raw material fresh oil: 2 h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ raw material fresh oil ratio by volume: 400

15 The second catalyst bed:

Reaction temperature: 170°C

Reaction pressure: 1.3MPa

Hydrogen/ raw material fresh oil ratio by volume: 200

The average results of 200 hour evaluation are shown in Table 3'.

20 [Example 2']

1. Catalyst production

a. Production of the catalyst of the first catalyst bed

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 450 °C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

b. Production of the catalyst of the second catalyst bed

10 1L of the support alumina was mixed with 2000g of aqueous solution of chloropalladic acid-nickel nitrate-magnesium nitrate containing 3.0g of palladium, 0.2g of nickel and 0.1g of magnesium, dried at 110°C for 8 hours and calcined at 550°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a temperature of 300°C to produce a palladium-based catalyst. The specific components of the catalyst are shown in Table 2'.

2. Catalyst evaluation

20 Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous manner. The material first passed through the first catalyst bed, and then through the second catalyst bed. The catalyst loading volume ratio of the two catalyst beds was 4:1. The operating conditions of the two reactors were as follows:

The first catalyst bed:

Reaction temperature: 150°C

Reaction pressure: 1.5MPa

Volume space velocity of raw material fresh oil: 2 h^{-1}

Liquid phase thermal cycle ratio: 4

Hydrogen/ raw material fresh oil ratio by volume: 400

The second catalyst bed:

5 Reaction temperature: 170°C

Reaction pressure: 1.3MPa

Hydrogen/ raw material fresh oil ratio by volume: 100

The average results of 200 hour evaluation are shown in Table 3'.

[Example 3']

10 1. Catalyst production

a. Production of the catalyst of the first catalyst bed

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 450°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour^{-1} for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

20 b. Production of the catalyst of the second catalyst bed

1L of the support catalyst was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 0.3g of Cu, dried at 110°C for 8 hours and calcined at 550°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The palladium-based catalyst precursor I in an oxidized state was reduced with

hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The specific components of the catalyst are shown in Table 2'.

2. Catalyst evaluation

- 5 Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous manner. The material from which heavy components were removed first passed through the first catalyst bed, and then through the second catalyst bed. The catalyst loading volume ratio of the two catalyst beds was 4:1.
- 10 The operating conditions of the two reactors were as follows:

The first catalyst bed:

Reaction temperature: 150°C

Reaction pressure: 1.5MPa

Volume space velocity of raw material fresh oil: 2 h⁻¹

- 15 Liquid phase thermal cycle ratio: 4

Hydrogen/ raw material fresh oil ratio by volume: 400

The second catalyst bed:

Reaction temperature: 170°C

Reaction pressure: 1.3MPa

- 20 Hydrogen/ raw material fresh oil ratio by volume: 100

The average results of 200 hour evaluation are shown in Table 3'.

[Example 4']

The process of Example 2 was repeated, except that in the production of the second catalyst:

1L of alumina was mixed with 600 of aqueous solution of phosphoric acid containing 60g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support.

1L of the above support was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor in an oxidized state.

The above palladium-based catalyst precursor in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 35°C to produce a palladium-based catalyst precursor in a reduced state.

1L of the above palladium-based catalyst precursor in a reduced state was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur and dried at 110°C to obtain a catalyst. The major components of the catalyst and the average results of 200 hour evaluation are respectively shown in Table 2' and Table 3'.

[Example 5']

The process of Example 2 was repeated, except that in the production of the catalyst in the second stage, specifically:

1L of alumina was mixed with 600 of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

1L of the above catalyst support containing P was mixed with 600g of aqueous solution of silica gel having a mass concentration of 5% of SiO₂, dried and calcined at 500°C to obtain a support containing P/SiO₂.

1L of the above support containing P/SiO₂ was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of

palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor in an oxidized state.

5 The above palladium-based catalyst precursor in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 35°C to produce a palladium-based catalyst precursor in a reduced state.

10 1L of the above palladium-based catalyst precursor in a reduced state was impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst and the average results of 200 hour evaluation are respectively shown in Table 2' and Table 3'.

[Example 6']

15 The process of Example 5' was repeated, except that in the production of the catalyst in the second stage, specifically:

1L of alumina was mixed with 600 of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for 4 hours to produce a catalyst support containing P.

20 1L of the above support containing P was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor in an oxidized state.

25 The above palladium-based catalyst precursor in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 35°C to produce a palladium-based catalyst precursor in a reduced state.

1L of the above palladium-based catalyst precursor in a reduced state was

impregnated with 550g of cyclohexane solution of tert-nonyl polysulfide containing 0.1g of sulphur to obtain a palladium-based catalyst. The major components of the catalyst and the average results of 200 hour evaluation are respectively shown in Table 2' and Table 3'.

5 [Example 7']

The process of Example 5' was repeated, except that in the production of the catalyst in the second stage, specifically:

1L of alumina was mixed with 600 of aqueous solution of phosphoric acid containing 27g of P, dried at 110°C for 8 hours and calcined at 400 °C for
10 4 hours to produce a catalyst support containing P.

1L of the above support containing P was mixed with 2000g of aqueous solution of chloropalladic acid-copper nitrate containing 3.0g of palladium and 1.0g of copper, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor in an oxidized state.

15 The above palladium-based catalyst precursor in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 35°C to produce a palladium-based catalyst.

The major components of the catalyst and the average results of 200 hour
20 evaluation are respectively shown in Table 2' and Table 3'.

[Example 8']

The process of Example 5' was repeated, except that in the production of the catalyst in the second stage, specifically:

1L of alumina was mixed with 600g of aqueous solution of phosphoric acid
25 containing 27g of P, dried at 110°C for 8 hours and calcined at 400°C for 4 hours to produce a catalyst support containing P.

1L of the above support containing P was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 500°C for 4 hours to produce a palladium-based catalyst precursor in an oxidized state.

- 5 The above palladium-based catalyst precursor in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 35°C to produce a palladium-based catalyst. The major components of the catalyst and the average results of 200 hour evaluation are respectively shown in Table 2' and Table 3'.

10 [Comparative Example 1']

1. Catalyst production

- 1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid-nickel nitrate containing 3.0g of palladium and 0.3g of nickel, dried at 110°C for 8 hours and calcined at 550°C for 4 hours to
15 produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

20 2. Catalyst evaluation

- Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous manner. The material from which heavy components were removed only passed through one catalyst bed. The catalyst loading of the one catalyst
25 bed was the same as that of two catalyst beds when employed. The specific operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 1.50MPa

Volume space velocity of raw material fresh oil: 2h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ raw material fresh oil ratio by volume: 400

5 The average results of 200 hour evaluation are shown in Table 3'.

[Comparative Example 2']

1. Catalyst production

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8
10 hours and calcined at 450 °C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major
15 components of the catalyst are shown in Table 2'.

2. Catalyst evaluation

Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous manner. The material from which heavy components were removed only
20 passed through one catalyst bed. The catalyst loading of the one catalyst bed was the same as that of two catalyst beds when employed. The specific operating conditions were as follows:

Reaction temperature: 150°C

Reaction pressure: 1.50MPa

25 Volume space velocity of raw material fresh oil: 2h⁻¹

Liquid phase thermal cycle ratio: 4

Hydrogen/ raw material fresh oil ratio by volume: 400

The average results of 200 hour evaluation are shown in Table 3'.

[Comparative Example 3']

5 1. Catalyst production

a. Production of the catalyst of the first catalyst bed

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid containing 3.0g of palladium, dried at 110°C for 8 hours and calcined at 450°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

15 b. Production of the catalyst of the second catalyst bed

1L of support alumina was mixed with 2000g of aqueous solution of chloropalladic acid- nickel nitrate containing 3.0g of palladium and 0.3g of nickel, dried at 110°C for 8 hours and calcined at 550°C for 4 hours to produce a palladium-based catalyst precursor I in an oxidized state. The above palladium-based catalyst precursor I in an oxidized state was reduced with hydrogen having a volume space velocity of 100 hour⁻¹ for 4 hours at a reduction temperature of 300°C to produce a palladium-based catalyst. The major components of the catalyst are shown in Table 2'.

2. Catalyst evaluation

25 Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous

manner. The material first passed through the first catalyst bed, and then through the second catalyst bed. The catalyst loading volume ratio of the two catalyst beds was 1:4. The operating conditions of the two reactors were as follows:

5 The first catalyst bed:

Reaction temperature: 150°C

Reaction pressure: 1.50MPa

Volume space velocity of raw material fresh oil: 2h⁻¹

Liquid phase thermal cycle ratio: 4

10 Hydrogen/ raw material fresh oil ratio by volume: 400

The second catalyst bed:

Reaction temperature: 170°C

Reaction pressure: 1.3MPa

Hydrogen/ raw material fresh oil ratio by volume: 400

15 The average results of 200 hour evaluation are shown in Table 3'.

[Comparative Example 4']

Production of the catalyst in Example 1' was repeated, except that in the Catalyst evaluation:

20 Hydrogenation operation of the hydrocarbon material comprising α,α -dimethylbenzyl alcohol in Table 1 was carried out in a continuous manner. The material first passed through the first catalyst bed, and then through the second catalyst bed. The catalyst loading volume ratio of the two catalyst beds was 4:1. The operating conditions of the two reactors were as follows:

The first catalyst bed:

Reaction temperature: 150°C

Reaction pressure: 1.50MPa

Volume space velocity of raw material fresh oil: 2h⁻¹

5 Liquid phase thermal cycle ratio: 0

Hydrogen/ raw material fresh oil ratio by volume: 400

The second catalyst bed:

Reaction temperature: 170°C

Reaction pressure: 1.3MPa

10 Hydrogen/raw material fresh oil ratio by volume: 200

The average results of 200 hour evaluation are shown in Table 3'.

Table 2': Major components of the catalyst

Number	Item	Al ₂ O ₃ g/L	Pd g/L	Metal auxiliary g/L	P g/L	S g/L	SiO ₂ g/L
Example 1'	First stage catalyst	568	2.87	0	0	0	0
	Second stage catalyst	556	2.79	Ni-0.34	0	0	0
Example 2'	First stage catalyst	554	2.78	0	0	0	0
	Second stage catalyst	556	2.83	Ni-0.24/ Mg-0.09	0	0	0

Example 3'	First stage catalyst	558	2.81	0	0	0	0
	Second stage catalyst	561	2.79	Cu-0.28	0	0	0
Example 4'	First stage catalyst	558	2.91	0	0	0	0
	Second stage catalyst	552	2.86	Cu-0.89	56.32	0.083	0
Example 5'	First stage catalyst	558	2.82	0	0	0	0
	Second stage catalyst	552	2.78	Cu-0.90	25.23	0.080	26
Example 6'	First stage catalyst	558	2.82	0	0	0	0
	Second stage catalyst	552	2.78	Cu-0.90	25.23	0.080	0
Example 7'	First stage catalyst	558	2.82	0	0	0	0
	Second stage catalyst	552	2.78	Cu-0.90	25.23	0	0
Example 8'	First stage catalyst	554	2.78	0	0	0	0
	Second stage catalyst	554	2.78	0	25.23	0	0
Comparative	Single	560	2.84	Ni-0.32	0	0	0

Example 1'	stage catalyst						
Comparative Example 2'	Single stage catalyst	563	2.76	0	0	0	0
Comparative Example 3'	First stage catalyst	551	2.77	0	0	0	0
	Second stage catalyst	548	2.84	Ni-0.33	0	0	0
Comparative Example 4'	First stage catalyst	568	2.87	0	0	0	0
	Second stage catalyst	556	2.79	Ni-0.34	0	0	0

Table 3' :

Item	Content of isopropylbenzene hydroperoxide in hydrogenation product ppm	Content of α -methylstyrene in hydrogenation product ppm	Content of dimerized isopropylbenzene ppm	Content of α,α -dimethylbenzyl alcohol in hydrogenation product ppm	Selectivity of isopropylbenzene %
Example 1'	0	12	86	186	99.82
Example 2'	0	8.6	67	146	99.87
Example 3'	0	5.8	78	85	99.83
Example 4'	0	3.2	51	54	99.92
Example 5'	0	2.5	48	32	99.95
Example 6'	0	4.8	58	68	99.90
Example 7'	0	5.1	62	71	99.88
Example 8'	0	5.3	66	75	99.86
Comparative Example 1'	18	350	412	46520	99.72
Comparative Example 2'	22	467	426	57368	99.64
Comparative Example 3'	0	12	245	4876	99.69
Comparative Example 4'	0	356	3250	123	99.12

It can be seen from Table 2' and Table 3':

- (1) According to the respective comparison between Comparative Examples 1'-2' and Example 1', and Example 3', in which both Comparative Examples 1'-2' employed a single catalyst bed filled with the same amount of catalyst, it can be seen that the content of isopropylbenzene hydroperoxide, the content of α -methylstyrene, the content of dimerized isopropyl benzene and the content of α,α -dimethylbenzyl alcohol in the

products of Comparative Examples 1'-2' were all higher than those in the examples, particularly the content of α,α -dimethylbenzyl alcohol. The above indicates that the method according to the present invention can achieve a high conversion to α,α -dimethylbenzyl alcohol.(2) According to the
5 comparison between Comparative Examples 3' and Example 1', in which the catalyst loading in the first catalyst bed in Comparative Example 3' was lower than that of the second catalyst bed, it can be seen that the content of dimerized isopropyl benzene and the content of α,α -dimethylbenzyl alcohol in the product of Comparative Examples 3' were significantly higher.

10 (3) According to the comparison between Examples 5' and Example 3', when phosphorus, silica and sulfur were introduced to the second catalyst simultaneously, the content of isopropylbenzene hydroperoxide, the content of α -methylstyrene, the content of dimerized isopropyl benzene and the content of α,α -dimethylbenzyl alcohol in the product of Examples 5' were
15 all lower than those in Example 3'.

(4) According to the comparison between Examples 6' and Example 5', when only phosphorus and sulfur were introduced to the second catalyst, the content of isopropylbenzene hydroperoxide, the content of α -methylstyrene, the content of dimerized isopropyl benzene and the content
20 of α,α -dimethylbenzyl alcohol in the product of Examples 6' were all higher than those in Example 5'.

(5) According to the comparison between Example 7' and Example 5', when only phosphorus was introduced to the second catalyst, the content of isopropylbenzene hydroperoxide, the content of α -methylstyrene, the
25 content of dimerized isopropyl benzene and the content of α,α -dimethylbenzyl alcohol in the product of Example 7' were all higher than those in Example 5'.

(6) According to the comparison between Examples 8' and Example 7', when only phosphorus was introduced to the second catalyst, the content of isopropylbenzene hydroperoxide, the content of α -methylstyrene, the
30

content of dimerized isopropyl benzene and the content of α,α -dimethylbenzyl alcohol in the product of Examples 8' were all higher than those in Example 7'.

- (7) According to the comparison between Comparative Example 4' and
- 5 Example 1', in which the liquid phase thermal cycle ratio of the first catalyst bed in the operating conditions of the reactor of Comparative Examples 4' was 0, it can be seen that the content of dimerized isopropyl benzene in the product of Comparative Examples 4' was significantly higher and the selectivity of isopropylbenzene was significantly lowered.

CLAIMS

1. A catalyst for producing isopropylbenzene from α,α -dimethylbenzyl alcohol,
5 comprising a support and an active component supported on the support,
wherein the support comprises a support substrate and a modifying auxiliary
component supported on the support substrate, wherein,
the active component includes metal palladium and/or oxides thereof,
the modifying auxiliary component includes phosphorus and/or oxides
10 thereof.
2. The catalyst according to claim 1, characterized in that the content of the
metal palladium and/or oxides thereof in the catalyst is 0.01-5wt%, preferably
0.05-1wt%, based on the content of the element palladium, and/or
15 the metal palladium has a dispersity of 5-10%, preferably 6.5-8.5%.
3. The catalyst according to claim 2, characterized in that the active
component further includes an active auxiliary metal and/or oxides thereof;
preferably, the active auxiliary metal is at least one selected from the group
20 consisting of metal copper, metal zinc, metal cobalt, metal tin, metal nickel
and metal silver;
preferably, the content of the active auxiliary metal and/or oxides thereof in
the catalyst is 0.0001-0.2wt%, more preferably 0.0007-0.2wt%, based on the
content of the auxiliary metal element therein.
25
4. The catalyst according to any one of claims 1 to 3, characterized in that the
content of the modifying auxiliary component in the catalyst is 0.2-20wt%,
preferably 1-15wt%, based on the content of element phosphorus.
- 30 5. The catalyst according to any one of claims 1 to 4, characterized in that,
the support substrate is at least one selected from the group consisting of

silica, alumina and activated carbon, and/or

the support substrate has a pore size of 10-25nm and a specific surface area of 50-180m²/g.

5 6. The catalyst according to any one of claims 1 to 5, characterized in that,
the catalyst further includes a co-catalyst; preferably, the co-catalyst is a
sulfur-containing compound; more preferably, the sulfur-containing
compound is derived from a sulfur-containing organic matter; further
preferably, the sulfur-containing organic matter is at least one selected from
10 the group of tert-nonyl polysulfides, tert-butyl polysulfides, thiophenes and
dimethyl disulfides etc.;

the content of the co-catalyst in the catalyst is preferably >0-1wt%, more
preferably >0-0.8wt%, wherein the amount of the co-catalyst is based on the
amount of effective elements therein, for example, the amount of element
15 sulfur.

7. The catalyst according to any one of claims 1 to 6, characterized in that,
when silica is not the support substrate, said modifying auxiliary component
further includes silica, which is preferably derived from silica gel, and
20 the content of silica in the catalyst is preferably >0-60wt%, more preferably
>0-40wt%.

8. The catalyst according to any one of claims 1 to 7, characterized in that,
when silica is not the support substrate, said modifying auxiliary component
25 further includes silica, wherein the molar ratio of the silicon to phosphorus
based on the element is ≤ 20 , preferably ≤ 10 , more preferably ≤ 4 , wherein, the
content of the modifying auxiliary component phosphorus and/or oxides
thereof in the catalyst is 0.2-20wt%, preferably 1-15wt%, more preferably
1-7wt%, wherein the content of phosphorus and/or oxides thereof is based on
30 the content of element phosphorus therein, and the silica content in the
catalyst is >0-60wt%, preferably >0-40wt%, for example, >0-20wt%.

9. A method for producing the catalyst according to any one of claims 1 to 8, comprising the following steps:

Step 1: an aqueous solution of a phosphorus-containing compound is mixed with a support substrate, dried and calcined to obtain a
5 phosphorus-containing support;

Step 2: the support is added to a solution of a palladium-containing compound, dried and calcined to obtain a catalyst precursor in an oxidized state;

Step 3: the catalyst precursor in an oxidized state is subjected to a reduction
10 treatment to obtain a catalyst.

10. The production method according to claim 9, characterized in that, the support substrate is at least one selected from the group consisting of silica, alumina and activated carbon, and/or

15 the palladium-containing compound is at least one selected from the group consisting of palladium chloride, palladium nitrate and chloropalladic acid, and/or

the phosphorus-containing compound is at least one selected from the group consisting of phosphoric acid, potassium dihydrogen phosphate, phosphorous
20 acid, calcium phosphate and ammonium hydrogen phosphate, etc., and/or

the solution in step 2 further comprises a compound containing an active auxiliary metal which is preferably at least one selected from the group consisting of active auxiliary metal chlorides, compounds of active auxiliary metal nitrates and compounds of active auxiliary metal acetates; more
25 preferably, the active auxiliary metal is at least one selected from the group consisting of metal copper, metal zinc, metal cobalt, metal tin, metal nickel and metal silver.

11. The production method according to either of claims 9 to 10,
30 characterized in that,

in step 1, step 2, the calcining temperature is 400-700°C, preferably 400-500°C, and/or

in step 3, a reduction treatment is carried out with hydrogen; preferably, the reduction temperature is 40-300°C, preferably 200-300°C, more preferably 250°C; the volume space velocity of hydrogen is 50-500h⁻¹, preferably 80-150h⁻¹.

5

12. The production method according to any one of claims 9 to 11, characterized in that step 1' is performed after step 1 and before step 2 :

Step 1': the phosphorus-containing support is mixed with an aqueous solution of silica gel, dried and calcined to obtain a support containing phosphorus and silicon.

10

13. The production method according to any one of claims 9 to 12, characterized in that the method further comprises step 4:

Step 4: the catalyst according to step 3 is added to a co-catalyst-containing solution and dried to obtain a further catalyst;

15

preferably, the co-catalyst is a sulfur-containing compound; more preferably, the sulfur-containing compound is derived from a sulfur-containing organic matter; further preferably, the sulfur-containing organic matter is at least one selected from the group of tert-nonyl polysulfides, tert-butyl polysulfides, thiophenes and dimethyl disulfides.

20

14. The production method according to any one of claims 9 to 13, characterized in that, based on 1L of the support substrate,

the amount of the palladium-containing compound is 0.06g/L-30g/L, preferably 0.5g/L-10g/L, based on the amount of element palladium therein, and/or

25

the amount of the compound containing an active auxiliary metal is 0.0006g/L-1.2g/L, preferably 0.01g/L-1.0g/L, based on the amount of the element of the active auxiliary metal therein, and/or

the amount of the phosphorus-containing compound is 2g/L-100g/L, preferably 5g/L-80g/L, based on the amount of element phosphorus therein, and/or

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the amount of the co-catalyst is 0.0001g/L-3g/L, preferably 0.01g/L-1g/L, more preferably 0.05g/L-0.2 g/L, wherein the amount of the co-catalyst is based on the amount of effective elements therein, such as element sulfur, and/or

- 5 the amount of silica gel is 6-300g/L, preferably 20-200g/L, wherein the amount of silica gel is based on the amount of silica therein.

15. The use of the catalyst according to any one of claims 1 to 8 or the catalyst obtained by the method according to any one of claims 9 to 14 in the
10 production of isopropylbenzene from α,α -dimethylbenzyl alcohol.

16. A method for producing isopropylbenzene from α,α -dimethylbenzyl alcohol, which is carried out in the presence of a palladium catalyst, preferably the catalyst according to any one of claims 1 to 8 or the catalyst
15 obtained by the method according to any one of claims 9 to 14; more preferably, the production method comprises: bring raw material in contact with hydrogen to react in the presence of the catalyst to obtain isopropylbenzene, wherein the method preferably employs a liquid phase thermal cycle process; more preferably, the cycle ratio is 1-10, preferably
20 4-8.

17. The production method according to claim 16, characterized in that the raw material comprise a hydrocarbon material comprising α,α -dimethylbenzyl alcohol, wherein the hydrocarbon material optionally
25 comprises isopropylbenzene, acetophenone, α -methylstyrene and dimerized isopropyl benzene, and optionally comprises isopropylbenzene hydroperoxide; preferably, the hydrocarbon material comprising α,α -dimethylbenzyl alcohol comprises an inert solvent, preferably isopropylbenzene and α,α -dimethylbenzyl alcohol.

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18. The production method according to claim 17, characterized in that a pressure is 0.1-4.0MPa, a temperature is 130-220°C, a liquid hourly space

velocity is $1-20\text{ h}^{-1}$, and a molar ratio of hydrogen to α,α -dimethylbenzyl alcohol is > 4 in the production method;

preferably, the pressure is $0.5-3.0\text{MPa}$, the temperature is $150-200^{\circ}\text{C}$, the liquid hourly space velocity is $4-15\text{ h}^{-1}$, and the molar ratio of hydrogen to α,α -dimethylbenzyl alcohol is > 5 .

19. The production method according to claims 16-18, comprising obtaining the isopropylbenzene from raw material of a hydrocarbon material comprising α,α -dimethylbenzyl alcohol and hydrogen through a first catalyst bed and a second catalyst bed in series, preferably by a liquid phase thermal cycle process;

wherein,

the catalyst loading of the first catalyst bed is greater than or equal to that of the second catalyst bed; preferably, the ratio by volume of the catalyst loading of the first catalyst bed to the catalyst loading of the second catalyst bed is $(1-6): 1$, preferably $(2-4): 1$;

the inlet temperature of the first catalyst bed is not higher than the inlet temperature of the second catalyst bed; preferably the first catalyst bed has a reaction temperature of $130-190^{\circ}\text{C}$, a reaction pressure of $0.1-5\text{MPa}$, and a liquid hourly space velocity of $1.0-20\text{h}^{-1}$, and/or the second catalyst bed has a reaction temperature of $150-230^{\circ}\text{C}$, a reaction pressure of $0.1-5\text{ MPa}$, and a liquid phase volume space velocity of $2.0-10\text{h}^{-1}$,

the liquid phase thermal cycle ratio of the first catalyst bed is preferably $1-10$; the liquid phase thermal cycle ratio of the second catalyst bed is preferably $0-2$.

20. The production method according to claim 19, wherein, in the first catalyst bed, the ratio by volume of hydrogen to the liquid phase is $300-1000$, preferably $400-800$, and/or in the second catalyst bed, the ratio by volume of hydrogen to the liquid phase is $100-800$, preferably $200-400$.

21. The production method according to claims 19-20, wherein,

- the catalyst of the first catalyst bed comprises metal Pd and/or oxides, and a support, and/or the catalyst of the second catalyst bed comprises metal Pd and/or oxides, a metal auxiliary and/or oxides thereof, and a support; preferably, the metal auxiliary is at least one selected from the group
- 5 consisting of Fe, Co, Ni, Ca, Mg and Cu, more preferably at least one selected from the group consisting of Cu, Ni and Mg, or
- the catalyst of the first catalyst bed and/or the catalyst of the second catalyst bed are the catalysts according to any one of claims 1 to 8.
- 10 22. The use of the method according to any one of claims 16-21 in the production of propylene oxide.