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(56) Related Art
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Abstract

The present invention relates to a process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas, and this process mainly solves the technical
5 problems of low hydrogen removal ratio and high CO loss existing in the prior art. In this invention, a hydrogen-containing CO mixed gas is used as the raw material, which passes through a catalyst layer having a gradually increased activity gradient in a reactor with a molar ratio of oxygen to hydrogen contained in the raw material being 0.5 to 5: 1, and at a reaction temperature of from 100 to 300 °C, a volume space velocity of from
10 100 to 10000 h⁻¹, and a reaction pressure of from -0.08 to 5.0 MPa, wherein the hydrogen in the reaction effluent is oxidized to water. The process of this invention is applicable in the industrial production of oxidative dehydrogenation of a CO mixed gas.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title: A PROCESS FOR SELECTIVE OXIDATIVE DEHYDROGENATION OF A HYDROGEN-CONTAINING CO MIXED GAS

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

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A PROCESS FOR SELECTIVE OXIDATIVE DEHYDROGENATION OF A HYDROGEN-CONTAINING CO MIXED GAS

Technical Field

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The present invention relates to a process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas, and particularly a process for selective oxidative dehydrogenation of a raw gaseous material for the preparation of an oxalate by CO coupling.

10

Background Art

Oxalates are important organic industrial chemicals and are substantially used for production of various dyes, medicaments, important solvents, extracting agents and intermediates in refined chemical industry. In the 21st century, oxalates, as degradable, environmentally friendly engineering plastic monomers, receive extensive international recognition. In addition, normal-pressure hydrolysis of an oxalate gives oxalic acid, and normal-pressure aminolysis gives oxalamide, which is a high-quality, sustained-release chemical fertilizer. An oxalate is also useful as a solvent and for the production of an intermediate of a pharmaceutical or dye, through, for example, various condensation reactions with fatty acid esters, cyclohexyl acetophenone, amino-alcohols and a good many heterocyclic compounds. It can also be used for synthesizing thymine used as a medical hormone. Further, low-pressure hydrogenation of an oxalate gives ethylene glycol, which is an extremely important industrial chemical. However, ethylene glycol is currently predominantly prepared by petroleum route, and is thus costly. China needs to import an enormous quantity of ethylene glycol each year, and the imported ethylene glycol in the year 2007 was up to 4.8 million tons.

A traditional process for producing an oxalate comprises esterification of oxalic acid with an alcohol. This process requires a high cost of production, consumes a lot of energy, produces serious contamination and inappropriately uses the raw material. Thus, the production of oxalates by the carbon monoxide coupling technique has become a hot issue in world-wide researches.

35

As generally known, carbon monoxide can be isolated and extracted from various carbon monoxide-containing mixed gases. The raw gaseous materials industrially useful for the isolation of carbon monoxide include natural gas, the synthetic gas converted from petroleum, water gas, semi water gas, tail gases from iron and steel plants, calcium carbide plants and phosphor plants, and the like. The main currently-
5 available method for isolating CO is a pressure-varying adsorption. Several companies in China have developed new pressure-varying adsorption techniques for isolating carbon monoxide. In particular, the highly efficient adsorbers as developed have an extremely high adsorption capacity and selectivity to carbon monoxide, and are thus
10 capable of solving the difficult problem of isolating high-purity carbon monoxide from a raw gaseous material having a high nitrogen or methane content. It is consequently possible to design and build a large-size carbon monoxide isolation facility. Nevertheless, the carbon monoxide isolated from a synthetic gas using this technique generally has a hydrogen content of more than 1 %, if a satisfactory yield of carbon
15 monoxide must be ensured. However, study shows that the presence of hydrogen results in a decreased catalytic activity of the catalyst used in the posterior CO coupling reaction, until the reaction stops. Thus, it is technically significant to develop the technique of selective dehydrogenation of carbon monoxide.

20 The currently available oxidative dehydrogenation techniques are predominantly oxidative dehydrogenation of hydrocarbons at elevated temperatures, but there are few documents or publications concerning the oxidative dehydrogenation of a hydrogen-containing carbon monoxide gas. For example, the patent CN96118939.8 discloses a process for the preparation of ethylene by oxidative dehydrogenation of ethane. The
25 catalyst used in said patent (CN96118939.8) is $\text{Na}_2\text{WO}_4\text{-Mn}_2\text{O}_3$ (wherein S is selected from the group consisting of SiO_2 , TiO_2 (rutile), MgO and the like), which can produce an ethane conversion and ethylene selectivity of more than 70 % at a relatively high space velocity, a suitable ethane to oxygen ratio and a proper reaction temperature, wherein the ethylene yield is generally more than 50 %. In the meantime, said patent
30 (CN96118939.8) merely mentions a single bed layer and does not mention a composite bed reactor.

Taking the patent CN03810160.2 as another example, it discloses a catalyst for the production of olefins from paraffinic hydrocarbons by oxidative dehydrogenation
35 (ODH). According one preferred embodiment of this patent (CN03810160.2), the

catalyst used in the ODH method comprises a base metal, a metal as a co-catalyst and a support comprising a plurality of discrete structures. In said patent (CN03810160.2), the base metal is defined as a non-Group VIII metal, except iron, cobalt and nickel. Suitable base metals include Group IB metals, Group VIIB metals, Group IIIA metals, Group VA metals, lanthanide metals, iron, cobalt and nickel. Suitable co-catalyst metals include Group VIII metals (i.e., platinum, palladium, ruthenium, rhodium, erbium and iridium). In some embodiments, the support is made from a refractory material. Suitable refractory materials for the support include aluminum oxides, stable aluminum oxides, zirconium dioxide, titanium dioxide, yttrium oxides, anhydrous silicic acid, niobium oxides and vanadium oxides. Likewise, said patent (CN03810160.2) only mentions a single bend layer and does not mention a composite bed reactor.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Summary of the Invention

According to a first aspect, the present invention provides a process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas, comprising using a hydrogen-containing CO mixed gas as the raw material and allowing said raw material to pass through a catalyst layer having a gradually increased activity gradient in a reactor with a molar ratio of oxygen to hydrogen contained in the raw material being 0.5 to 5: 1, and at a reaction temperature of from 100 to 300 °C, a volume space velocity of from 100 to 10000 h⁻¹, and a reaction pressure of from -0.08 to 5.0 MPa, wherein the hydrogen in the reaction effluent is oxidized to water.

Unless the context clearly requires otherwise, throughout the description and the claims, the words “comprise”, “comprising”, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

The technical problem to be solved by the present invention is to provide a new process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas because in the prior art the selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas has a high CO loss and a low hydrogen removal ratio. This process has the advantages of a low CO loss and a high hydrogen removal ratio.

In order to solve the above-mentioned technical problem, the present invention employs the following solutions: a process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas, comprising using a hydrogen-containing CO mixed gas as the raw material and allowing said raw material to pass through a catalyst layer having a gradually increased activity gradient in a reactor with a molar ratio of oxygen to hydrogen contained in the raw material being 0.5 to 5: 1, and at a reaction temperature of from 100 to 300 °C, a volume space velocity of from 100 to 10000 h⁻¹, and a reaction pressure of from -0.08 to 5.0 MPa, wherein the hydrogen in the reaction effluent is oxidized to water.

In one preferred embodiment (I), said catalyst layer having a gradually increased activity gradient is disposed in a composite bed reactor and comprises catalyst I and catalyst II, wherein said catalyst I and catalyst II both comprise at least one active component selected from platinum metals, the amount of the active component in catalyst I is lower than the amount of the active component in catalyst II, and the ratio of catalyst I to catalyst II is from 0.1 to 5: 1, preferably from 0.1 to 3: 1.

In another preferred embodiment (II), said catalyst layer having a gradually increased activity gradient is disposed in a mixed bed reactor and comprises an insert filler and catalyst III comprising platinum metals as active component, wherein the ratio of the inert filler to the catalyst III is from 0.1 to 5: 1, preferably from 0.1 to 3: 1.

In the above-mentioned embodiments (I) and (II), catalysts I, II and III all comprise at least one of a silicon oxide, an aluminum oxide and a molecular sieve, preferably an aluminum oxide, as the support. The active components of catalysts I, II and III are all selected from platinum and palladium of the platinum metals, and are preferably palladium. Said catalysts I, II and III may optionally comprise additional dopant metals, such as Ba, Fe, Zn, Lanthanides, Li and/or Mn. Relative to the weight of the support, the amount of the active component of said catalyst I is from 0.005 to 0.1 %

by weight, preferably from 0.01 to 0.1 % by weight, the amount of the active component of said catalyst II is from 0.1 to 1.5 % by weight, preferably from 0.1 to 1 % by weight, and the amount of the active component of said catalyst III is from 0.05 to 1.5 % by weight, preferably from 0.05 to 1.0 % by weight. Said inert filler is an insert aluminum oxide, porcelain bead or stainless steel filler, preferably an insert aluminum oxide or porcelain bead.

In the above embodiments, the preferable reaction conditions are a reaction temperature of from 150 to 280 °C, a volume space velocity of from 800 to 8000 h⁻¹, and a reaction pressure of from 0 to 2.0 MPa, and the more preferred reaction conditions are a reaction temperature of from 180 to 260 °C, a volume space velocity of from 1000 to 6000 h⁻¹, and a reaction pressure of from 0 to 1.0 MPa. The percent by volume of hydrogen in the hydrogen-containing CO gaseous material is higher than 0 to 10 %, preferably 0.01 to 5 %. In the composite bed reactor, the ratio of catalyst I to catalyst II preferably ranges from 0.1: 1 to 3: 1. In the mixed bed reactor, the ratio of the inert filler to catalyst III preferably ranges from 0.1: 1 to 3: 1. The molar ratio of oxygen to hydrogen contained in the raw material preferably ranges from 0.5 to 3: 1.

As generally known, carbon monoxide and hydrogen are both gases having relatively strong reductibility. When they are present together with oxygen, selective oxidative dehydrogenation typically occurs together with a reaction of CO which results in a relatively big loss of CO. There exist even some cases where only CO reacts but hydrogen does not. Thus, it is a challenging task to develop a high-selectivity dehydrogenation process in the presence of CO. We have found out, after conducting a lot of researches, that little or no CO loss is observed in the process of the present invention for selective dehydrogenation in the presence of carbon monoxide, and the residual hydrogen can be ≤ 8 ppm, preferably ≤ 5 ppm, particularly preferably ≤ 1 ppm. Further dynamic studies show that during the process of the present invention for highly selective dehydrogenation of a hydrogen-containing CO gas, the adsorption rate of hydrogen to a catalytic active center is far higher than the adsorption rate of CO, and the reaction activation energy of the step of reacting CO with oxygen to generate CO₂ is far higher than that of the step of reacting hydrogen with oxygen to generate water. This provides an important theoretical basis and support, from the angle of reaction kinetics, for the maximum transformation of hydrogen and, at the same time, the utmost avoidance of CO loss resulting from oxidation.

Likewise, as generally known, the reaction of hydrogen with oxygen is a strongly exothermic reaction, and dynamic studies show that the rate of the hydrogen/oxygen reaction is closely associated with the distribution of the active components of the catalysts. The higher the distribution percentage of the active components is per one unit
5 of support specific area, the higher the reaction rate is and the higher a local temperature rise is. The higher the temperature is, the higher the probability for CO to react with oxygen is and the higher the CO loss is. Thus, it is a technically crucial point for decreasing the CO loss to keep the reaction procedure balanced and prevent an overly high local temperature rise so as to avoid CO loss.

10 In the above-mentioned embodiment (I) of the present invention, a composite bed reactor is used. The distribution concentration of the catalytic active components is relatively low at the inlet of the reactor, and then increases gradually. This, on one hand, avoids an overly high rate of reaction between hydrogen and oxygen at the inlet of the
15 reactor, and on the other hand, sufficiently ensures the hydrogen removal ratio thanks to an increased concentration of active components downstream of the reactor, hence achieving the object of effectively increasing the hydrogen removal ratio and significantly decreasing the CO loss.

20 In the above-mentioned embodiment (II) of the present invention, a mixed bed reactor is used. An inert filler is filled in this reactor together with a catalyst. This not only effectively decreases the distribution concentration of the active components in one volume unit of the reactor bed layer to effectively avoid an overly high local reaction
25 rate, but also effectively expedites the heat transfer and decentralizes the heat thanks to the introduction of the inert filler, which acts as a heat carrier, hence avoiding an overly high CO loss resulting from an overly high local temperature rise. In this invention, the inert filler and catalyst may be filled into the mixed bed reactor in many ways, and the ratio of the inert filler to the catalyst may be high at the inlet of the reactor, and then gradually decreases along the catalyst bed layer. In the technical solution of the present
30 invention, the distribution concentration of the catalytic active components is relatively low at the inlet of the reactor, and then increases gradually. This, on one hand, avoids an overly high rate of reaction between hydrogen and oxygen at the inlet of the reactor, and on the other hand, sufficiently ensures the hydrogen removal ratio thanks to an increased concentration of active components downstream of the reactor, hence achieving the
35 object of effectively increasing the hydrogen removal ratio and significantly decreasing

the CO loss.

By using the technical solution of the present invention, the CO loss is lower than 1 %, and the residual hydrogen can be ≤ 8 ppm, preferably ≤ 5 ppm, particularly
5 preferably ≤ 1 ppm. It can be seen that a superior technical effect is achieved.

The CO loss set forth in the present invention is calculated according to the following equation:

10
$$\text{CO loss} = (\text{the mass of CO in the raw material} - \text{the mass of CO in the product}) / \text{the mass of CO in the product} \times 100 \%$$

The present invention will be further illustrated by, but are not limited to, the following Examples.

15

Specific Embodiments

Example 1

20 Catalyst Preparation:

100 g Aluminum oxide support with a specific surface area of $50 \text{ m}^2/\text{g}$ was taken to formulate a catalyst according to the content of 0.05% Pd/Al₂O₃. The steps are as follows: palladium nitrate was taken to formulate an impregnation liquid according to
25 the palladium load. The aluminum oxide support was impregnated with this liquid for 10 hours and then dried in vacuum for 12 hours to obtain a solid. The solid was then dried at 120 °C for 4 hours, calcined at 450 °C for 6 hours and then reduced with hydrogen at 300 °C for 4 hours to form the desired 0.05% Pd/Al₂O₃ (the active components are calculated based on percent by weight, the same below), catalyst I.

30

The desired 0.5% Pd/Al₂O₃ (the active components are calculated based on percent by weight, the same below), catalyst II, was prepared according to the above steps.

Catalysts I and II were respectively taken in desired amounts according to a ratio of
35 catalyst I to catalyst II of 1: 1, and catalyst II and catalyst I were then filled into a reactor

in turn. A CO gaseous material having a hydrogen content of 1 % by volume (the same below) was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.8: 1, and at a reaction temperature of 150 °C, a volume space velocity of 500 h⁻¹, and a reaction pressure of 3.0 MPa in the composite bed reactor. The reaction results (measured with an HP7890 gas chromatograph and a TCD detector, the same below) were a CO loss of 0.3 % and a hydrogen content of 1 ppm in the reaction effluent.

10 Example 2

0.08% Pd/Al₂O₃, catalyst I and 0.8% Pd/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

15 Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 2: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 3 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 2: 20 1, and at a reaction temperature of 180 °C, a volume space velocity of 1500 h⁻¹, and a reaction pressure of 2.0 MPa in the composite bed reactor. The reaction results were a CO loss of 0.5 % and a hydrogen content of 3 ppm in the reaction effluent.

25 Example 3

0.02% Pd/Al₂O₃, catalyst I and 1.2% Pd/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

30 Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 0.2: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 0.3 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 5: 1, and at a reaction temperature of 200 °C, a volume space velocity of 5000 h⁻¹, 35 and a reaction pressure of 0.05 MPa in the composite bed reactor. The reaction results

were a CO loss of 0.6 % and a hydrogen content of 0 in the reaction effluent.

Example 4

- 5 0.1% Pd + 0.6% Ba + 0.2% Fe/silicon oxide, catalyst I and 1.0% Pd + 0.2% Zn/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

Catalysts I and II were respectively taken in desired amounts according to a ratio of
10 catalyst I to catalyst II of 0.4: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 0.8 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 1: 1, and at a reaction temperature of 240 °C, a volume space velocity of 6000 h⁻¹,
15 and a reaction pressure of -0.05 MPa in the composite bed reactor. The reaction results were a CO loss of 0.4 % and a hydrogen content of 5 ppm in the reaction effluent.

Example 5

- 20 0.08% Pd + 0.4% Fe/ZSM-5 (a silicon to aluminum ratio of 500: 1), catalyst I and 0.80% Pd + 0.2% La/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

Catalysts I and II were respectively taken in desired amounts according to a ratio of
25 catalyst I to catalyst II of 0.8: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 2 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 280 °C, a volume space velocity of 8000 h⁻¹, and
30 a reaction pressure of -0.02 MPa in the composite bed reactor. The reaction results were a CO loss of 0.2 % and a hydrogen content of 6 ppm in the reaction effluent.

Example 6

- 35 0.08% Pd/Al₂O₃, catalyst I and 0.60% Pd + 0.2% Fe/Al₂O₃, catalyst II were prepared

according to the process described in Example 1 for preparing catalysts.

Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 0.5: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 5 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 1.5: 1, and at a reaction temperature of 200 °C, a volume space velocity of 3000 h⁻¹, and a reaction pressure of 0.2 MPa in the composite bed reactor. The reaction results were a CO loss of 0.8 % and a hydrogen content of 8 ppm in the reaction effluent.

Example 7

0.07% Pd + 0.3% Li/Al₂O₃, catalyst I and 0.60% Pd + 0.2% Mn/ZSM-5 (a silicon to aluminum ratio of 200: 1), catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 4: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 8 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 190 °C, a volume space velocity of 2000 h⁻¹, and a reaction pressure of 0.8 MPa in the composite bed reactor. The reaction results were a CO loss of 0.5 % and a hydrogen content of 5 ppm in the reaction effluent.

Example 8

0.09% Pd/Al₂O₃, catalyst I and 0.80% Pd/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 0.3: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 0.2 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn

and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 220 °C, a volume space velocity of 5000 h⁻¹, and a reaction pressure of 0.3 MPa in the composite bed reactor. The reaction results were a CO loss of 0.2 % and a hydrogen content of 0 in the reaction effluent.

5

Example 9

0.06% Pt/Al₂O₃, catalyst I and 0.40% Pd/Al₂O₃, catalyst II were prepared according to the process described in Example 1 for preparing catalysts.

10

Catalysts I and II were respectively taken in desired amounts according to a ratio of catalyst I to catalyst II of 0.2: 1, and catalyst II and catalyst I were then filled into a reactor in turn. A CO gaseous material having a hydrogen content of 0.2 % was used as the raw material. The raw material was contacted with catalyst I and catalyst II in turn and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 220 °C, a volume space velocity of 5000 h⁻¹, and a reaction pressure of 0.3 MPa in the composite bed reactor. The reaction results were a CO loss of 0.1 % and a hydrogen content of 0 in the reaction effluent.

15

Comparative Example 1

The steps described in Example 1 were carried out under the same conditions described therein, except that only catalyst II was used as the catalyst. At the same total space velocity, oxygen to hydrogen ratio, reaction temperature and reaction pressure, the reaction results were a CO loss of 0.88 % and a hydrogen content of 15 ppm in the reaction effluent.

25

It can be seen that the CO loss in Example 1 is significantly lower than that in Comparative Example 1, and the hydrogen removal ratio in Example 1 is much higher than that in Comparative Example 1.

30

Example 10

Catalyst Preparation:

5 100 g Aluminum oxide support with a specific surface area of 50 m²/g was taken to formulate a catalyst according to the content of 0.5% Pd/Al₂O₃. The steps are as follows: palladium nitrate was taken to formulate an impregnation liquid according to the palladium load. The aluminum oxide support was impregnated with this liquid for 10 hours and then dried in vacuum for 12 hours to obtain a solid. The solid was then dried
10 at 120 °C for 4 hours, calcined at 450 °C for 6 hours and then reduced with hydrogen at 300 °C for 4 hours to form the desired 0.5% Pd/Al₂O₃ catalyst.

An aluminium oxide was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 0.5: 1 to 0.1: 1 from the inlet to the outlet of
15 the reactor. A CO gaseous material having a hydrogen content of 1 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.8: 1, and at a reaction temperature of 150 °C, a volume space velocity of 500 h⁻¹,
20 and a reaction pressure of 3.0 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.3 % and a hydrogen content of 1 ppm in the reaction effluent.

Example 11

25 0.8% Pd/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

An aluminium oxide was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 1: 1 to 0.1: 1 from the inlet to the outlet of
30 the reactor. A CO gaseous material having a hydrogen content of 3 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 2: 1, and at a reaction temperature of 180 °C, a volume space velocity of 1500 h⁻¹,
35 and a reaction pressure of 2.0 MPa in the mixed bed reactor. The reaction results were a

CO loss of 0.4 % and a hydrogen content of 3 ppm in the reaction effluent.

Example 12

- 5 1.2% Pd/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

An inert porcelain bead was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 2: 1 to 0.8: 1 from the inlet to the outlet of
10 the reactor. A CO gaseous material having a hydrogen content of 0.3 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 5: 1, and at a reaction temperature of 200 °C, a volume space velocity of 5000 h⁻¹,
15 and a reaction pressure of 0.05 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.5 % and a hydrogen content of 0 in the reaction effluent.

Example 13

- 20 0.1% Pd + 0.6% Ba + 0.2% Fe/silicon oxide catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

An inert porcelain bead was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 2: 1 to 0.2: 1 from the inlet to the outlet of
25 the reactor. A CO gaseous material having a hydrogen content of 0.8 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 1: 1, and at a reaction temperature of 240 °C, a volume space velocity of 6000 h⁻¹,
30 and a reaction pressure of -0.05 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.3 % and a hydrogen content of 5 ppm in the reaction effluent.

Example 14

- 35 0.8% Pd + 0.4% Fe/ZSM-5 (a silicon to aluminum ratio of 500: 1) catalyst was prepared

according to the process described in Example 10 for preparing a catalyst.

5 A stainless steel filler was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 4: 1 to 0.1: 1 from the inlet to the outlet of the reactor. A CO gaseous material having a hydrogen content of 2 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 280 °C, a volume space velocity of
10 8000 h⁻¹, and a reaction pressure of -0.02 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.2 % and a hydrogen content of 6 ppm in the reaction effluent.

Example 15

15 0.6% Pd/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

A stainless steel filler was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 5: 1 to 0.6: 1 from the inlet to the outlet of
20 the reactor. A CO gaseous material having a hydrogen content of 5 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 1.5: 1, and at a reaction temperature of 200 °C, a volume space velocity of
25 3000 h⁻¹, and a reaction pressure of 0.2 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.6 % and a hydrogen content of 8 ppm in the reaction effluent.

Example 16

30 0.60% Pd + 0.2% Mn/ZSM-5 (a silicon to aluminum ratio of 200: 1) catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

An inert aluminum oxide was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 1: 1 to 0.5: 1 from the inlet to the
35 outlet of the reactor. A CO gaseous material having a hydrogen content of 8 % by

volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 190 °C, a volume space velocity of 2000 h⁻¹, and a reaction pressure of 0.8 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.5 % and a hydrogen content of 5 ppm in the reaction effluent.

Example 17

0.2% Pt/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

A stainless steel filler was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 2: 1 to 0.3: 1 from the inlet to the outlet of the reactor. A CO gaseous material having a hydrogen content of 0.2 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 220 °C, a volume space velocity of 5000 h⁻¹, and a reaction pressure of 0.3 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.2 % and a hydrogen content of 0 in the reaction effluent.

Example 18

0.1% Pt/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

An inert porcelain bead was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of 2: 1 to 0.8: 1 from the inlet to the outlet of the reactor. A CO gaseous material having a hydrogen content of 0.2 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material being 0.6: 1, and at a reaction temperature of 220 °C, a volume space velocity of 5000 h⁻¹, and

a reaction pressure of 0.3 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.3 % and a hydrogen content of 1 ppm in the reaction effluent.

Example 19

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0.8% Pt/Al₂O₃ catalyst was prepared according to the process described in Example 10 for preparing a catalyst.

10 An inert porcelain bead was used as the inert filler. The inert filler and the catalyst were filled at a gradually decreasing ratio of from 3: 1 to 0.5: 1 from the inlet to the outlet of the reactor. A CO gaseous material having a hydrogen content of 0.2 % by volume was used as the raw material. The raw material was contacted with the catalyst by passing through a mixed bed reactor filled with the inert filler and palladium-containing catalyst, and reacted, with a molar ratio of oxygen to hydrogen contained in the raw material
15 being 0.6: 1, and at a reaction temperature of 220 °C, a volume space velocity of 5000 h⁻¹, and a reaction pressure of 0.3 MPa in the mixed bed reactor. The reaction results were a CO loss of 0.1 % and a hydrogen content of 0 in the reaction effluent.

Comparative Example 2

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The steps described in Example 10 were carried out under the same conditions described therein, except that only palladium catalyst was used and no inert filler was used for dilution. At the same total space velocity, oxygen to hydrogen ratio, reaction temperature and reaction pressure, the reaction results were a CO loss of 0.9 % and a hydrogen
25 content of 13 ppm in the reaction effluent.

It can be seen that the CO loss in Example 10 is significantly lower than that in Comparative Example 2, and the hydrogen removal ratio in Example 10 is much higher than that in Comparative Example 2.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas, comprising using a hydrogen-containing CO mixed gas as the raw material and allowing said raw material to pass through a catalyst layer having a gradually increased activity gradient in a reactor with a molar ratio of oxygen to hydrogen contained in the raw material being 0.5 to 5: 1, and at a reaction temperature of from 100 to 300 °C, a volume space velocity of from 100 to 10000 h⁻¹, and a reaction pressure of from -0.08 to 5.0 MPa, wherein the hydrogen in the reaction effluent is oxidized to water.
2. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to claim 1, wherein the catalyst layer is disposed in a composite bed reactor and comprises catalyst I and catalyst II, wherein said catalyst I and catalyst II both comprise at least one active component selected from platinum metals and may optionally comprise additional dopant metals, such as Ba, Fe, Zn, Lanthanides, Li and/or Mn, the amount of the active component in catalyst I is lower than the amount of the active component in catalyst II, and the ratio of catalyst I to catalyst II is from 0.1 to 5.
3. A process according to claim 2 wherein the ratio of catalyst I to catalyst II is from 0.1 to 3: 1.
4. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to claim 1, wherein the catalyst layer is disposed in a mixed bed reactor and comprises an insert filler and catalyst III comprising platinum metals as active component, wherein said catalyst III may optionally comprise additional dopant metals and the ratio of the inert filler to catalyst III is from 0.1 to 5: 1.
5. A process according to claim 4 wherein said dopant metals are selected from Ba, Fe, Zn, Lanthanides, Li and/or Mn.
6. A process according to claim 4 or claim 5 wherein the ratio of the inert filler to catalyst III is from 0.1 to 3: 1.
7. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to claim 2 or claim 3, wherein said catalyst I and catalyst II both

comprise at least one of a silicon oxide, an aluminum oxide and a molecular sieve, as the support, wherein, relative to the weight of the support, the amount of the active component of said catalyst I is from 0.005 to 0.1 % by weight, and the amount of the active component of said catalyst II is from 0.1 to 1.5 % by weight.

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8. A process according to claim 7 wherein said molecular sieve is silicon oxide.

9. A process according to claim 7 or claim 8 wherein the amount of the active component of said catalyst I is from 0.01 to 0.1% by weight.

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10. A process according to any one of claim 7 to 9 wherein the amount of the active component of said catalyst II is from 0.1 to 1% by weight.

11. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of claims 4 to 6 wherein said catalyst III comprises at least one of a silicon oxide, an aluminum oxide and a molecular sieve as the support, wherein, relative to the weight of the support, the amount of the active component of said catalyst III is from 0.05 to 1.5 % by weight and said inert filler is an insert aluminum oxide, porcelain bead or stainless steel filler.

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12. A process according to claim 11 wherein said molecular sieve is silicon oxide.

13. A process according to claim 11 or claim 12 wherein the amount of the active component of said catalyst III is from 0.05 to 1.0% by weight.

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14. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of the preceding claims, wherein the reaction temperature is from 150 to 280 °C, the volume space velocity is from 800 to 8000 h⁻¹, and the reaction pressure is from 0 to 2.0 MPa.

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15. A process according to claim 14 wherein the reaction temperature is from 180 to 260°C.

16. A process according to claim 14 or claim 15 wherein the volume space velocity is from 1000 to 6000 h⁻¹.

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17. A process according to anyone of claims 14 to 16 wherein the reaction pressure is from 0 to 1.0 MPa.

18. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of the preceding claims, wherein the percent by volume of hydrogen in the hydrogen-containing CO gaseous material is higher than 0 to 10 %.
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19. A process according to claim 18 wherein the percent by volume of hydrogen in the hydrogen-containing CO gaseous material is higher than 0.01 to 5%
20. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of the preceding claims, wherein the molar ratio of oxygen to hydrogen contained in the raw material is 0.5 to 3: 1.
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21. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of the preceding claims, wherein the platinum metal active component is platinum or palladium.
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22. A process for selective oxidative dehydrogenation of a hydrogen-containing CO mixed gas according to any one of the preceding claims, wherein the CO mixed gas obtained after selective oxidative dehydrogenation has a hydrogen concentration of ≤ 8 ppm and a CO loss of < 1 %.
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23. A process according to claim 22 wherein the hydrogen concentration is ≤ 5 ppm.
24. A process according to claim 22 or claim 23 wherein the hydrogen concentration is ≤ 1 ppm.
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25. A process for selective oxidative dehydrogenation of hydrogen-containing CO mixed gas substantially as herein described with reference to any one of the examples but excluding comparative examples.