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(54) **Process for producing oxygen-containing hydrocarbon compounds.**

(57) Compounds containing oxygen, hydrogen and carbon having 1 or 2 carbon atoms can be prepared by reacting a gaseous mixture of carbon oxide and hydrogen in the presence of a catalyst composition comprising
(A) substantially metallic rhodium;
(B) an oxide of a metal of Group IIa, IIIa, IVa or Va of the Periodic Table of short form; and optionally
(C) an element selected from niobium, tantalum, chromium, manganese and rhenium when the metal oxide (B) is of a metal of Group IIIa, IVa or Va.

This catalyst composition is highly efficient under relatively mild reaction conditions and can be prepared easily and inexpensively.

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Title:

PROCESS FOR PRODUCING OXYGEN-CONTAINING HYDROCARBON COMPOUNDS

This invention relates to a process for producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms by reacting a gaseous mixture composed of carbon oxide and hydrogen in the presence of a hydrogenation catalyst. More specifically, this invention pertains to a process for advantageously producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms, particularly ethanol, from the aforesaid gaseous mixture using a catalyst composition comprising metallic rhodium and a certain metallic oxide as a hydrogenation catalyst.

In recent years, there has been a worldwide scarcity of oil resources, and it is anticipated that a balance between supply and demand of oils will be aggravated in near future. Naphtha derived from crude oils has become increasingly costly in recent years, and the cost of production of low-boiling olefins, acetic acid, acetaldehyde, ethanol, etc., which are the basic products of the petrochemical industry from naphtha, has tended to increase year by year. Accordingly, there has been an increasing need to develop a process for producing these basic raw materials of the petrochemical industry at low cost from a synthesis gas comprising a mixture of carbon monoxide and hydrogen.

Presently, the synthesis gas is produced industrially by steam-reforming of naphtha and natural gases, but it is expected that in near future synthesis gases from low-cost carbon resources occurring abunduntly throughout the world such as heavy oils, coals and oil sands will go into industrial production. The synthesis gas will therefore be an advantageous raw material both in cost and supply.

Extensive investigations have been made heretofore about the production of hydrocarbons or both hydrocarbons and oxygen-containing hydrocarbon compounds from a gaseous mixture of carbon oxide (carbon monoxide or carbon dioxide) and hydrogen (a synthesis gas process or a modified Fischer-Tropsch method). It has been reported, for example, that various oxygen-containing hydrocarbon compounds and hydrocarbons can be synthesized by reacting a synthesis gas comprising carbon monoxide and hydrogen in a ratio of from 4:1 to 1:4 in the presence of a hydrogenation catalyst comprising a metal of the iron group or noble metal group at a temperature of 150 to 450°C and a pressure of 1 to about 700 atmospheres (F. Fischer, H. Tropsch, Ber., 59,830, 832, 923 (1926), and H. Pichler, Adv. Catalysis, IV, 271 (1952)). The product obtained by this method is a mixture of oxygen-containing hydrocarbon compounds and hydrocarbons having 1 to 20 carbon atoms, and this method cannot afford industrially useful oxygen-containing hydrocarbon compounds having low carbon numbers selectively and efficiently.

As a method for synthesizing oxygen-containing hydrocarbon compounds and lower olefins from a synthesis gas, the Hydrocol method comprising performing the reaction at 300 to 350°C and 20 to 50 atmospheres using a catalyst composed of iron or cobalt supported on magnesium oxide, thorium oxide, etc. (see H. Pichler, Adv. Catalysis IV, 271 (1952)), and the Synthol method involving performing the reaction at 300 to 400°C and 70 to 250 atmospheres (F.Fischer, H. Tropsch, Brennstoff-Chem., 4, 276 (1923), 5, 201, 217 (1924), 7, 97, 299 (1926), 8, 65 (1927)) have already been known. These methods, however, have poor selectivity. They are advantageous for production of higher olefins, but cannot selectively give olefins having 2 to 4 carbon atoms and oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms which are useful as industrial materials.

On the other hand, as regards the use of a rhodium catalyst, a method was suggested which comprises contacting a synthesis gas at atmospheric pressure with a rhodium-supported catalyst containing a silica or alumina carrier or a rhodium metal plate to produce methane and not more than 10% of C_2-C_4 hydrocarbons (see M. A. Vannica, J. Catal., 37, 449 (1975), and B. Sexton, G.A: Somorjai, ibid. 46, 167 (1977)). Furthermore, about the selective production of oxygen-containing hydrocarbon compounds having low carbon numbers by reaction of a synthetic gas using a rhodium-supported catalyst, there were proposed a method which comprises reacting a synthetic gas at 290 to 325°C and 35 to 350 atmospheres while maintaining the CO/H_2 ratio at much higher than 1 and the flow rate of the reactant gas at $10^3 h^{-1}$ or higher as SV, to produce a mixture of oxygen-containing hydrocarbon compounds having low carbon numbers, especially acetic acid, acetaldehyde and ethanol, in a carbon efficiency, based on the consumed carbon monoxide, of 50% (Belgian Patent No. 824822, TD No. 2503233, and Japanese Laid-Open Patent Publication No. 80806/76); and a method which comprises reacting a synthesis gas at a flow rate of at least 10^3 h^{-1} under a pressure of 50 to 300 atmospheres using a silica carrier catalyst containing rhodium and iron to produce methanol and ethanol at substantially the same carbon efficiency as in the aforesaid method (see Belgian Patent No. 824823, and Japanese Laid-Open Patent Publication No. 80807/76). These methods give methanol and ethanol in a substantially equimolar ratio, but cause formation of large amounts of methane or hydrocarbons having 2 or more carbon atoms as by-products. At a low CO concentration in the synthesis gas (CO/H_2=1.0 or less), a low pressure (1 to 50 atmospheres) or a low flow rate (not more than 10^2 h^{-1} as SV) which are advantageous conditions for economical industrial processes, by-product hydrocarbons tend to increase further in these methods, and the selectivity for industrially useful oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms such as ethanol is drastically reduced.

According to an improved method involving use of a catalyst comprising both rhodium and manganese (see Japanese Laid-Open Patent Publication No. 14706/77), an increase in the conversion of CO per unit weight of rhodium is noted, but the addition of manganese can scarcely increase the selectivity for the formation of oxygen-containing hydrocarbon compounds. It has been pointed out that the addition of an excessive amount of manganese rather increases formation of hydrocarbons and reduces the selectivity for the formation of the desirable oxygen-containing hydrocarbon compounds.

A method has also been known for producing a mixture of methanol and ethanol from a synthesis gas by reacting it at 1 to 50 atmospheres and 150 to 300°C using a catalyst obtained by supporting a rhodium cluster or platinum cluster on an oxide of at least one metal selected from metals of Groups IIab, IIIab and IVab of the periodic table of short form (see Japanese Laid-Open Patent Publications Nos. 41291/79 and 44605/79). Although the catalyst used in this method is highly active, this method still has various difficulties which have to be overcome. For example, catalyst preparation requires the use of a special and expensive noble metal carbonyl cluster compound as a raw material, and includes operation in an inert atmosphere (in vacuum or in an inert gas). The catalyst has a short lifetime under high-temperature and high-pressure conditions which are required for achieving a high conversion, and there is a limit to the operable temperature range for the catalyst.

In view of the prior art techniques discussed above, it has been desired to develop a rhodium-containing catalyst which is suitable for selective production of oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms, particularly ethanol, at a high carbon efficiency under relatively mild low-pressure reaction conditions. The use of such a rhodium-containing catalyst will provide a new technique which supersedes synthesis of methanol from a synthesis gas or production of ethylene from naphtha.

It is an object of this invention to provide a process for producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms at a high carbon efficiency from a gaseous mixture of carbon oxide and hydrogen using a rhodium-containing catalyst which is relatively inexpensive and is easily available.

Another object of this invention is to provide a process for producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms, especially ethanol, from a gaseous mixture of carbon oxide and hydrogen.

Other objects and advantages of this invention will become apparent from the following description.

It has now been found in accordance with this invention that when a catalyst composition consisting basically of (A) substantially metallic rhodium and (B) an oxide of a metal (to be referred to as a "metal oxide") selected from metals of Groups IIa, IIIa, IVa and Va of the periodic table of short form is used in the production of oxygen-containing hydrocarbon compounds by reacting a gaseous mixture composed of carbon oxide and hydrogen, the carbon efficiency of the oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms is markedly improved, and reaches 50% or more. It has also been found that the catalyst composition used in this invention generally has a wide operating temperature range, and exhibits superior catalytic activity at a wide temperature range of from about 100 to about 400^{o}C, and its catalytic activity lasts for an extended period of time even under high-temperature high-pressure reaction conditions.

According to one aspect of this invention, there is provided a process for producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms which comprises reacting a gaseous mixture consisting of carbon oxide and hydrogen in the presence of a hydrogenation catalyst, said hydrogenation catalyst being a catalyst composition comprising

(A) substantially metallic rhodium, and

(B) an oxide of a metal selected from metals of Groups IIa, IIIa, IVa and Va of the periodic table of short form.

In the present specification and the appended claims, the term "oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms" denotes hydrocarbons having 1 or 2 carbon atoms and an oxygen atom, such as methanol, ethanol, formaldehyde, acetaldehyde, formic acid and acetic acid.

The term "carbon oxide" inclusively represents both carbon monoxide (CO) and carbon dioxide (CO_2). In the present invention carbon monoxide and carbon dioxide are used either singly or as a mixture. Preferably, the carbon oxide is carbon monoxide.

The "periodic table of short form", as used in the present application, denotes a periodic table of the type described at page 738 of "Encyclopaedia Chimica", Vol. 5 (1951), Kyoritsu Shuppan K.K., Tokyo, Japan. According to this periodic table, Group IIa includes Be, Mg, Ca, Sr, Ba and Ra; Group IIIa, Sc, Y, lanthanide elements and actinide elements; Group IVa, Ti, Zr and Hf; and Group Va, V, Nb and Ta.

The term "carbon efficiency of oxygen-containing hydrocarbon compounds", as used in this application, denotes the percentage of the oxygen-containing hydrocarbon compounds in moles based on the consumed carbon oxide calculated for carbon (on the carbon basis).

The term "selectivity for ethanol", as used in this application, denotes the percentage of ethanol based on the resulting oxygen-containing hydrocarbon compounds calculated for carbon, (on the carbon basis).

The metallic oxide used in the catalyst composition in accordance with this invention is an active catalytic ingredient having the ability to increase synergistically the catalytic activity of metallic rhodium which is a main catalytic ingredient. At the same time, the metal oxide serves as a carrier for metallic rhodium. The catalyst composition preferably consists essentially of metallic rhodium and the aforesaid metal oxide.

Examples of the metal oxide include magnesium oxide, calcium oxide, beryllium oxide, lanthanum oxide, cerium oxide, neodymium oxide, yttrium oxide, zirconium oxide, titanium oxide, thorium oxide, vanadium oxide, niobium oxide and tantalum oxide. Of these, lanthanum oxide, neodymium oxiee, cerium oxide, yttrium oxide, thorium oxide, titanium oxide, zirconium oxide, niobium oxide, and tantalum oxide are preferred. Thorium oxide, titanium oxide, zirconium oxide, niobium oxide and tantalum oxide are especially preferred.

These metal oxides can be used either singly or in combination with each other. In order to support metallic rhodium, the metal oxide may generally be a solid in the form of powder, granule, pellet or lump having a surface area of generally at least 1 m^2/g, preferably 10 to 1000 m^2/g.

Deposition of metallic rhodium on the metal oxide can be effected by any customary method so long as substantially all of the rhodium deposited on the metal oxide is metallic. Advantageously, this can be performed using a simple organic or inorganic salt of rhodium. The "simple salt of rhodium", as referred to herein, means a compound simply containing mono- or -di-nuclear rhodium element, and is clearly distinct from the cluster compound of rhodium mentioned hereinabove. Specific examples of the simple salt of rhodium include inorganic salts of rhodium such as the chloride, nitrite and carbonate of rhodium, and organic salts of rhodium such as the acetate, oxalate, ethylenediamine complex

$(Rh(NH_2C_2H_4NH_2)_3)Cl_3$, pyridine complex $(Rh(C_4H_4N)_4Cl_3)$, acetylacetonato salt, cyclooctadiene complex, dicyclopentadienyl complex, π-allyl complex, and allene complex of rhodium.

Deposition of metallic rhodium on the metal oxide from these rhodium salts may be performed, for example, by a method which comprises dissolving the rhodium salt in a suitable solvent (for example, water, an alcohol such as methanol or ethanol, an ether such as tetrahydrofuran or dioxane, or a hydrocarbon such as hexane or benzene), impregnating the metal oxide with the resulting solution, removing the solvent, and then heat-treating the impregnated metal oxide in an atmosphere of a reducing gas such as hydrogen gas or synthesis gas under atmospheric ortelevared pressures until substantially all of the impregnated rhodium salt is converted to metallic rhodium (for example, at a temperature of about 50 to about 500°C for about 10 minutes to about 2 days; this reducing treatment can be performed in a reactor prior to the performance of the process of this invention); or chemically reducing the impregnated metal rhodium salt with a reducing agent such as formaldehyde, hydrazine, metal hydrides (e.g., sodium hydride or potassium hydride), metal borohydrides (e.g., sodium borohydride), or complex metal hydrides (e.g., lithium aluminum hydride). As a result, there can be obtained a catalyst composition in accordance with this invention in which substantially metallic rhodium is supported and combined with the metal oxide.

The content of metallic rhodium is not critical, and can be widely varied depending upon the type or shape of the metal oxide used, etc. Generally, it is advantageous that the content of metallic rhodium is about 0.0001 to about 50% by weight, preferably about 0.01 to about 25% by weight, more preferably about 0.1 to about 10% by weight, based on the weight of the catalyst composition.

The catalyst composition consisting essentially of metallic rhodium and the metal oxide so prepared can be directly used in the process of this invention. In accordance with this invention, it has been found that the joint use of the metallic rhodium and metal oxide with silica gives further increased catalytic activity, and a very high selectivity for ethanol. This discovery is surprising in view of the fact that the conjoint use of metallic rhodium and the metal oxide with alumina which is frequently used as a catalyst carrier results in reduced catalytic activity.

Accordingly, an especially preferred catalyst composition in accordance with this invention consists essentially of metallic rhodium,the metal oxide and silica. This preferred catalyst composition may comprise silica as a substrate and deposited thereon, metallic rhodium and the metal oxide; or an intimate composite of silica and the metal oxide, and metallic rhodium deposited on the composite.

In the case of the former type, deposition of metallic rhodium and the metal oxide on silica can be performed by any method known per se. Deposition of metallic rhodium can be performed by the method described hereinabove. On the other hand, deposition of the metal oxide can be performed, for example, by dissolving an inorganic or organic metal compound of a metal of Groups IIa, IIIa, IVa and Va of the periodic table of short form in a suitable solvent (for example, water, an alcohol such as methanol or ethanol, an ether such as tetrahydrofuran or dioxane, or a hydrocarbon such as hexane or benzene), impregnating the resulting solution in silica in various forms such as a powder, pellet, granule or lump, removing the solvent, and then heat-treating the impregnated silica in an atmosphere of an oxygen-containing gas (e.g., air), an inert gas (e.g., nitrogen, argon, helium, or carbon dioxide gas), or a reducing gas (e.g., hydrogen or synthesis gas) depending upon the type of the metal compound used until substantially all of the impregnated metal compound is converted to the corresponding metal oxide (for example, heating it at a temperature of about 100 to about 600°C for about 30 minutes to about 2 days). As a result, the metal oxide can be deposited on silica.

The inorganic or organic metal compound used in the deposition of the metal oxide includes the chlorides, oxynitrates, nitrates, carbonates, hydroxides, acetates, formates, oxalates, silyl ether salts, acetylacetonate salts, polyhydroxystearates, alkoxides, dicyclopentadienyl complexes, π-allyl complexes, benzyl complexes, and allene complexes of metals of Groups IIa, IIIa, IVa and Va of the periodic table of short form.

Specific examples of these inorganic or organic metal compounds are magnesium chloride ($MgCl_2$), magnesium bromide ($MgBr_2$), magnesium nitrate ($(Mg(NO_3)_2$), magnesium hydroxide ($Mg(OH)_2$), magnesium carbonate ($MgCO_3$), magnesium formate ($Mg(HCOO)_2$), magnesium oxalate ($MgC_2O_4 \cdot 2H_2O$), magnesium chlorate ($Mg(ClO_4)_2$), magnesium methoxide ($Mg(OCH_3)_2$), magnesium ethoxide ($Mg(OC_2H_5)_2$), magnesium propoxide ($Mg(OC_3H_7)_2$), magnesium butoxide ($Mg(OC_4H_9)_2$), magnesium methylcarbonate ($Mg(CH_3OCOO)_2$), calcium chloride ($CaCl_2$), calcium bromide ($CaBr_2$), calcium formate ($Ca(HCOO)_2$), calcium oxalate ($CaC_2O_4 \cdot 2H_2O$), calcium hydroxide ($Ca(OH)_2$), calcium ethoxide ($Ca(OC_2H_5)_2$) , calcium butoxide ($Ca(OC_4H_9)_2$), beryllium chloride ($BeCl_2$), beryllium ethoxide ($Be(OC_2H_5)_2$), beryllium formate ($Be(HCOO)_2$), lanthanum chloride ($LaCl_3 \cdot 3H_2O$), lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$), lanthanum oxalate ($La_2(C_2O_4)_3 \cdot nH_2O$), lanthanum acetate ($La(CH_3CO_2)_2 \cdot 4H_2O$), lanthanum acetylacetonate ($La(C_5H_7O_2)_3 \cdot H_2O$), lanthanum carbonate ($La_2(CO_3)_3$), neodymium chloride ($NdCl_3 \cdot 3H_2O$), neodymium bromide ($NdCl_3$), neodymium nitrate ($Nd(NO_3)_3 \cdot 3H_2O$), neodymium acetate ($Nd(CH_3COO)_3 \cdot nH_2O$), neodymium acetylacetonate ($Nd(C_5H_7O_2)_3 \cdot H_2O$), yttrium chloride ($YCl_3$), yttrium chlorate ($Y(ClO_3)_3 \cdot 9H_2O$), yttrium perchlorate ($Y(ClO_4)_3 \cdot 9H_2O$), yttrium carbonate ($Y_2(CO_3)_3 \cdot 3H_2O$), yttrium ammonium carbonate ($(NH_4)Y(CO_3)_2 \cdot H_2O$), yttrium formate ($Y(HCOO)_3 \cdot 2H_2O$), yttrium tartrate ($Y_2(C_4H_4O_5)_3 \cdot nH_2O$), yttrium acetylacetonate ($Y(C_5H_7O_2)_3 \cdot H_2O$), cerium chloride ($CeCl_3 \cdot 7H_2O$), cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$), cerium acetate ($Ce(CH_3CO_2)_3 \cdot H_2O$), cerium acetylacetonate ($Ce(C_5H_7O_2)_3$), cerous ammonium nitrate ($Ce(NO_3)_2 \cdot 2(NH_4NO_3) \cdot 4H_2O$), ceric ammonium nitrate ($Ce(NO_3)_4 \cdot 2(NH_4NO_3) \cdot nH_2O$), cerium carbonate ($Ce_2(CO_3)_3 \cdot 8H_2O$), cerium oxalate ($Ce_2(C_2O_4)_3 \cdot 9H_2O$), zirconium oxynitrate ($ZrO(NO_3)_2 \cdot 2H_2O$), zirconum nitrate ($Zr(NO_3)_3 \cdot 6H_2O$), titanium nitrate ($Ti(NO_3)_3 \cdot 6H_2O$), zirconium oxyacetate ($ZrO(CH_3COO)_3$), titanium oxyacetate ($TiO(CH_3COO)_3$), zirconium oxychloride ($ZrOCl_2$), titanium oxychloride ($TiOCl_2$), zirconium tetrachloride ($ZrCl_4$), titanium tetrachloride ($TiCl_4$), zirconium acetate ($Zr(CH_3COO)_2$), titanium acetate ($Ti(CH_3COO)_2$), zirconium ethoxide ($Zr(OC_2H_5)_4$), titanium ethoxide ($Ti(OC_2H_5)_4$), zirconium isopropoxide ($Zr(O\text{-}isoC_3H_7)_4$), titanium isopropoxide ($Ti(O\text{-}isoC_3H_7)_4$), zirconium n-propoxide ($Zr(On\text{-}C_3H_7)_4$), titanium n-propoxide ($Ti(On\text{-}C_3H_7)_4$), zirconium butoxide ($Zr(OC_4H_9)_4$), titanium butoxide ($Ti(OC_4H_9)_4$), dicyclopentadienyl zirconium chloride ($(\pi\text{-}C_5H_5)_2ZrCl_2$), dicyclopentadienyl titanium chloride ($(\pi\text{-}C_5H_5)TiCl_2$), dicarbonyldicyclopentadienyl zirconium ($(\pi\text{-}C_5H_5)_2Zr(CO)_2$), dicarbonyldicyclopentadienyl titanium ($(\pi\text{-}C_5H_5)_2Ti(CO)_2$), zirconium acetylacetonate ($Zr(C_5H_7O_2)_4$), titanium acetylacetonate ($Ti(C_5H_7O_2)_4$), thorium nitrate ($Th(NO_3)_4 \cdot 5H_2O$), thorium acetylacetonate ($Th(C_5H_7O_2)_4$), thorium chloride ($ThCl_4$), thorium acetate ($Th(CH_3COO)_2$), thorium isopropoxide ($Th(iso\text{-}C_3H_7O)_4$), thorium n-propoxide ($Th(n\text{-}C_3H_7O)$), thorium butoxidd ($Th(C_4H_9O)_4$), vanadyl ethoxide ($VO(O\ C_2H_5)_3$), vanadyl butoxide ($VO(OC_4H_9)_3$), vanadyl methoxide ($VO(OCH_3)_3$), vanadyl ethoxychloride ($VO(OC_2H_5)_2Cl$), vanadyl acetylacetone ($VO(C_5H_7O_2)_3$), niobium propoxide ($Nb(OC_3H_7)_5$), niobium ethoxide ($Nb(OC_2H_5)_5$), niobium butoxide ($Nb(OC_4H_9)_5$), niobium acetylacetonate ($Nb(C_5H_7O_2)_3$), vanadocene ($(\pi\text{-}C_5H_5)_2V$), niobucene ($Nb(\pi\text{-}C_5H_5)_2X_2$; X=Cl, CO, H), tantalum ethoxide ($Ta(OC_2H_5)_5$), tantalum butoxide ($Ta(O\ C_4H_9)_5$), tantalum acetylacetonate ($Ta(C_5H_7O_2)_3$), niobium chloride ($NbCl_5$), tantalum chloride ($TaCl_5$), π-allyl vanadium carbonyl complex ($(\pi\text{-}C_3H_5)_2\ V(CO)_2$), π-allyl tantalum carbonyl complex ($(\pi\text{-}C_3H_5)_2\ Ta(CO)_2$) and benzyl zirconium complex ($Zr(CH_2C_6H_5)_4$).

These metal compounds are generally converted to metal oxides by heat-treatment and/or photo-decomposition in an atmosphere containing an oxygen-containing gas, an inert gas or a reducing gas.

In what condition the metal oxide is deposited on and combined with silica is not clear. It is assumed however that because of a chemical reaction between the metal compound used as a raw material and the hydroxyl group on the surface of silica, at least a part of the deposited metal oxide is in the form of a fixed oxide in which the metal in the metal compound is chemically bonded to a silicon atom through oxygen. It should be understood therefore that the "metal oxide", as used in this invention, also embraces such a fixed oxide.

Deposition of metallic rhodium and deposition of the metal oxide can be performed in various sequences depending upon the depositing conditions. For example, when the deposition of the metal oxide is carried out in an atmosphere containing an oxygen-containing gas or an inert gas, it is generally preferred to perform the deposition of the metal oxide first. When the deposition of the metal oxide is carried out in an atmosphere of a reducing gas, the deposition of metallic rhodium and the deposition of the metal oxide can be performed simultaneously or sequentially in an optional order.

The silica on which to deposit metallic rhodium and the metal oxide may have a surface area of generally at least 10 m^2/g, preferably 10 to 1000 m^2/g, more preferably 50 to 500 m^2/g. It may assume various ordinary forms as a catalyst substrate, such as a powder, granule, pellet, or lump.

The preferred catalyst composition may also be in such a form that metallic rhodium is deposited on a composite of silica and the metal oxide. The composite of silica and the metal oxide can be usually produced by preparing an aqueous solution of a water-soluble silicon compound and a water-soluble metal compound of the type exemplified hereinabove, co-precipitating silicon and the metal in the form of hydroxide from the aqueous solution in a customary manner, separating the co-precipitate, optionally molding it into such a shape as granule or pellet, and then firing it. Deposition of metallic rhodium on the resulting silica-metal composite can be performed by the method described hereinabove.

The resulting catalyst composition comprising metallic rhodium, the metal oxide and silica may contain metallic rhodium in a proportion of generally about 0.0001 to about 50% by weight, preferably about 0.01 to about 25% by weight, more preferably about 0.1 to about 10% by weight, based on the weight of the catalyst composition. The weight ratio of metallic rhodium to the metal oxide is generally from 1:100 to 100:1, preferably from 1:50 to 50:1, more preferably from 1:10 to 10:1, and the weight ratio of the metal oxide to silica is generally from 1000:1 to 1:1000, preferably from 100:1 to 1:100, more preferably from 10:1 to 1:10. The content of silica may be about 0.001 to about 99% by weight, preferably about 0.1 to about 98% by weight, more preferably about 1 to about 90% by weight, based on the weight of the catalyst composition.

It has further been found in accordance with this invention that the carbon efficiency of the oxygen-containing hydrocarbon compound having 1 or 2 carbon atom and the selectivity for ethanol can be further improved by incorporating an element selected from niobium, tantalum, chromium, manganese and rhenium as a sub-main catalyst ingredient into a catalyst composition consisting of metallic rhodium, an oxide of a metal selected from metals of Groups IIIa, IVa and Va of the periodic table of short form, and optionally silica and using the resulting catalyst composition in the reaction of a gaseous mixture of hydrogen and carbon oxide.

Thus, according to another aspect of this invention, there is also provided a process for producing oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms which comprises reacting a gaseous mixture composed of carbon oxide and hydrogen in the presence of a hydrogenation catalyst, said hydrogenation catalyst being a catalyst composition comprising

(i) substantially metallic rhodium,

(ii) an element selected from the group consisting of niobium, tantalum, chromium, manganese and rhenium, and

(iii) an oxide of a metal selected from the group consisting of metals of Groups IIIa, IVa and Va of the periodic table of short form, and

(iv) optionally, silica.

The catalyst composition used in this process can be prepared in the same way as in the aforesaid catalyst composition except that the metal element selected from niobium, tantalum, chromium, manganese and rhenium is additionally deposited on the metal oxide, or silica, or the silica-metal oxide composite.

Deposition of such additional metal element on the metal oxide, silica or the silica-metal oxide composite can be performed in the same way as in the deposition of metallic rhodium. For example, it can be performed by dissolving an inorganic or organic salt or alkoxide of the metal element in a suitable solvent (for example, water, an alcohol such as methanol or ethanol, an ether such as tetrahydrofuran or dioxane, or a hydrocarbon such as hexane or benzene), impregnating the resulting solution in the metal oxide, silica or the silica-metal oxide composite, removing the solvent, and reducing the impregnated metal salt until substantially all of it is reduced to metallic element as in the case of metallic rhodium.

The inorganic or organic salt or alkoxide of the additional metal element that can be used includes, the chlorides, nitrates, carbonates, acetates, oxalates, acetylacetonate salts, dicyclopentadienyl complexes, π-allyl complexes, allene complexes and alkoxides of the metals. Specific examples include rhenium chloride ($ReCl_5$), rhenium bromide ($ReBr_5$), rhenium carbonyl ($(Re_2(CO)_{10}$), dicyclopentadienyl rhenium hydride ($((\pi-C_5H_5)_2ReH_3$), carbonyl dicyclopentadienyl rhenium ($((\pi-C_5H_5)_2Re(CO)_2$), rhenium nitrate ($Re(NO_3)_5 \cdot 6H_2O$), rhenium acetate ($Re(CH_3COO)_5$), ammonium rhenate ($((NH_4)_2Re_2O_4$), niobium chloride ($NbCl_5$), niobium bromide ($NbBr_5$), dicyclopentadienyl niobium hydride ($((\pi-C_5H_5)_2NbH_3$), π-allyl niobium ($((\pi-C_3H_5)_4Nb$), tantalum chloride ($TaCl_5$), tantalum bromide ($TaBr_5$), dicyclopentadienyl tantalum hydride ($(\pi-C_5H_5)_2TaH_3$), π-allyl tantalum ($((\pi-C_3H_5)_4Ta$), niobium acetylacetonate ($Nb(C_5H_7O_2)_5$), tantalum acetylacetonate ($Ta(C_5H_7O_2)_5$), manganese chloride ($MnCl_2 \cdot 4H_2O$), manganese acetylacetonate ($Mn(C_5H_7O_2)_2$), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$), manganese nitrate ($Mn(NO_3)_2 \cdot 6H_2O$), dicyclopentadienyl manganese ($((C_5H_5)_2Mn$), chromium chloride ($CrCl_3$, or $CrCl_3 \cdot 6H_2O$), chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), chromium acetylacetonate ($Cr(C_5H_7O_2)_3$), dicyclopentadienyl chromium ($Cr(C_5H_5)_2$), and π-allyl chromium ($((\pi-C_3H_5)_3Cr$). These metal compounds can be used either singly or in combination with each other.

Deposition of such a metal element can be performed either before, during or after the deposition of metallic rhodium.

The amount of the metal element to be deposited is not critical, and can be varied widely depending upon the type of the metal element,etc. Generally, it is such that the weight ratio of metallic rhodium to the metal element is from 50:1 to 1:50 preferably from 20:1 to 1:20 more preferably from 1:10 to 10:1. The total amount of metallic rhodium and the metal element may be about 0.001 to about 50% by weight, preferably about 0.01 to about 25% by weight, more preferably about 0.1 to about 25% by weight, based on the weight of the catalyst composition.

The reaction of a gaseous mixture of carbon oxide and hydrogen in the presence of the catalyst composition of the various embodiments described hereinabove can be performed in a manner known per se. For example, the reaction can be performed by feeding the catalyst composition into a suitable catalytic reactor such as a closed circulating reactor, a fixed bed type reactor adapted for flowing of a starting gaseous mixture at atmospheric or elevated pressure a batchwise pressure reactor or a batchwise shaking pressure reactor, and contacting the starting gaseous mixture with the catalyst composition at about 50^{o} to about $450^{o}C$ and a space velocity of about 10 to about 10^{6} liters/liter.hr^{-1}, preferably about 10^{2} to about 10^{5} liters/liter.hr^{-1}, at a temperature of about 100 to about $350^{o}C$, and a pressure of about 0.5 to about 350 atmospheres (G), preferably about 1 to about 300 atmospheres (G).

The mole ratio of carbon oxide to hydrogen in the starting gaseous mixture to be fed into the reactor is generally from 20:1 to 1:20, preferably from 1:5 to 5:1, more preferably from 1:2 to 2:1.

Thus, according to the process of this invention, oxygen-containing hydrocarbon compounds having 1 or 2 carbon atoms can be produced with a high carbon efficiency from a gaseous mixture of carbon oxide and hydrogen by using the aforesaid catalyst composition which is easily available commercially and has excellent catalytic activity and selectivity. The process of this invention gives oxygen-containing hydrocarbon compounds containing methanol and/or ethanol as main ingredients. The mixture of methanol and ethanol formed as main ingredients can be easily separated into the constituents by distillation. Hence, the process of this invention is commercially feasible for production of methanol and ethanol. Moreover, blending of the oxygen-containing hydrocarbon compounds containing methanol and ethanol as main ingredients with a fuel gas gives fuels which may supersede the present fuels from natural resources and are expected to contribute to saving of petroleum resources.

One great advantage of the process of this invention is that ethanol can be produced at a high selectivity when the aforesaid catalyst composition or the aforesaid silica-containing catalyst composition further includes a metal element selected from niobium, tantalum, chromium, manganese and rhenium in addition to metallic rhodium.

Ethanol can be easily separated from the oxygen-containing hydrocarbon compounds containing a major proportion of ethanol which are obtained by the process of this invention. Hence, the process of this invention is commercially feasible for production of ethanol from a synthesis gas. Moreover, blending of the oxygen-containing hydrocarbon compounds containing ethanol as a main ingredient with a fuel gas or gasoline gives fuels which may supersede the present fuels from natural resources and are expected to contribute to saving of petroleum resources.

The following examples specifically illustrate the present invention. It should be noted however that the present invention is in no way limited by these examples.

The various abbreviations and terms appearing in the following examples have the following meanings.

RG: Reagent grade

SV: Space velocity defined as follows:

$$SV = \frac{\text{Amount of the feed gas (ml/hr)}}{\text{Amount of catalyst (ml) x time (hr)}}$$

Feed: Amount of feed gas (ml/hr)

C_1: methane

C_2: ethane + ethylene

C_3: propane + propylene

C_4: butane + butene

Tr: trace amount

CE: carbon efficiency (%) of oxygen-containing hydrocarbon compounds defined as follows:

$$CE = \frac{\text{Moles of methanol + (moles of ethanol) + moles of acetaldehyde + moles of acetic acid) x 2 + (moles of propanol) x 3 + (moles of butanol) x 4}}{\text{Moles of carbon oxide reacted}} \times 100$$

Selectivity for ethanol (%):

$$\frac{\text{(moles of ethanol formed) x 2}}{\text{Moles of the oxygen-containing hydrocarbon compounds formed (on carbon basis)}} \times 100$$

STY: Space time yield

STY of the oxygen-containing hydrocarbon compounds is expressed by the following equation.

$$STY = \frac{\text{Weight of the oxygen-containing hydrocarbon compounds (grams)}}{\text{(weight of the catalyst charged (kg))} \times \text{time (hours)}}$$

Example 1

Rhodium chloride trihydrate (0.50 g) was dissolved in 100 cc of distilled water, and 20 g of magnesium oxide powder (RG; a product of Nakarai Chemical Co., Ltd.) was added to the aqueous solution to impregnate the magnesium oxide with the aqueous solution. The impregnated magnesium oxide was evaporated to dryness by a rotary evaporator to afford a yellow powder. The resulting yellow powder was packed into a closed circulating-type reactor (total capacity 400 ml), heat-treated under vacuum at 200°C, and then subjected to reducing treatment in a stream of hydrogen at 350°C for 15 hours. After reduction, a gaseous mixture consisting of carbon monoxide and hydrogen introduced into the reactor and the reaction was started under the conditions shown in Table 1 (this reaction will be referred to hereinbelow as a $CO-H_2$ reaction). When the activity of the catalyst became steady, the distribution of products of the $CO-H_2$ reaction was examined. The results are shown in Table 1.

Examples 2 to 10

By the same operation as in Example 1, rhodium was deposited on 20g of titanium oxide powder (a product of Merck; RG), zirconium oxide powder (a product of Nakarai Chemical Co., Ltd.; RG), lanthanum oxide powder (a product of Kishida Cheic Cheic Chemical Co., Ltd.; RG), neodymium oxide powder (a product of Wako Pure Chemical Co., Ltd.; RG), cerium oxide powder (99% pure, a product of Wako Pure Chemical Co., Ltd.), yttrium oxide powder (a product of Wako Pure Chemical Co., Ltd.; Rg), thorium oxide powder (a product of Tokyo Chemical Co., Ltd.; RG), niobium oxide powder (a product of Wako Pure Chemical Co., Ltd; RG), and tantalum oxide powder, respectively, using an aqueous solution of 0.50 g of rhodium chloride trihydrate in 100 cc of distilled water. Using the resulting catalysts, the $CO-H_2$ reaction was performed in the same way as in Example 1. The results are shown in Table 1.

The products in vapor phase were analyzed by gas chromatography using a thermal conducting detector (TCD) and an active carbon column (1 m, room temperature, and an Al_2O_3-dimethylformamide (supported in an amount of 38% by weight) column (4 m, room temperature). The oxygen-containing hydrocarbon compounds trapped by a dry ice acetone trap of the reactor were analyzed by TCD gas chromatography on a Porapak Q (trademark) column (4 m, 200°C) and a PEG-1500 column (2m, 80°C).

Comparative Example 1

In the same way as in the preceding Examples, rhodium was deposited on 20 g of silica (WAKOW-GEL, 200 m^2/g, C-200) and γ-alumina (Nishio Kogyo K.K., 280 m^2/g, A-11), and using the resulting catalyst, the $CO-H_2$ reaction was performed in the same way as in the preceding Examples. The results are shown in Table 1.

It is seen that with the rhodium on silica or on γ-alumina, oxygen-containing hydrocarbon compounds were not formed, or formed only in traces.

Table 1

Example	Catalyst	Reaction conditions: Temperature (°C)	Partial pressure (mmHg) CO	Partial pressure (mmHg) H_2	Time (hours)
1	MgO-Rh (Rh 0.20 g)	245 240 260	20 30 30	45 32 35	23 23.5 48
2	TiO-Rh (Rh 0.20 g)	210 232	20 32	45 33	48 14
3	ZrO_2-$RhCl_3$ (Rh 0.20 g)	185 200	20 30	45 35	48 39
4	La_2O_3-Rh (Rh 0.20 g)	235 202 198	20 20 20	45 45 45	6.8 23.5 47.5
5	Nd_2O_3-Rh (Rh 0.20 g)	198 220	20 20	45 45	43 18
6	CeO_2-Rh (Rh 0.20 g)	210 190	20 20	45 45	15 23
7	Y_2O_3-Rh (Rh 0.20 g)	220 195	20 20	45 45	14 46
8	ThO_2-Rh (Rh 0.20 g)	185 210	20 30	45 30	15 23
9	Nb_2O_5-Rh (Rh 0.20 g)	195 210	20 20	45 45	15 19
10	Ta_2O_5-Rh (Rh 0.20 g)	195 210	20 20	45 45	25 12
Comparative Example 1	γ-Al_2O_3-Rh (Rh 0.20 g)	220	20	45	23
	SiO_2-Rh (Rh 0.20 g)	235	20	42	48

- to be continued -

Table - 1 (continued)

Example	Amounts (m-moles) of the products						CE (%)
	CH_3OH	C_2H_5OH	CH_3CHO	Other oxygen-containing hydrocarbon compounds (*1)	C_1	Other hydro-carbons (*2)	
1	0.66 0.78 0.88	0.28 0.084 0.134	- - -	- - -	0.91 0.65 0.82	0.11 0.14 0.23	52 50 46
2	± ±	0.28 0.23	0.28 0.15	+ +	0.70 0.46	0.41 0.27	34 43
3	0.23 0.184	0.37 0.32	0.086 0.22	+ 0.013	0.422 0.63	0.06 0.176	66 56
4	0.53 0.51 1.23	0.19 0.085 0.17	+ + +	- - -	0.49 0.44 0.57	0.25 0.02 0.08	43 59 68
5	1.58 0.67	0.28 0.18	+ +	- -	0.52 0.85	0.04 0.21	75 45
6	0.27 0.34	0.14 0.18	0.03 0.01	0.01 0.01	0.67 0.48	0.23 0.15	34 49
7	0.51	0.15 1.06	0.01 0.08	+ -	0.79 0.59	0.21 0.10	37 57
8	0.16 0.13	0.18 0.24	0.01 0.02	+ +	0.48 0.54	0.06 0.10	43 44
9	0.02 0.01	0.12 0.20	0.03 0.03	0.01 0.02	0.59 0.98	0.06 0.19	30 26
10	0.08 0.02	0.16 0.24	0.02 0.02	+ +	0.54 0.69	0.16 0.24	32 30
Comparative Example 1	- 0.01	- 0.03	- 0.04	- +	0.45 0.38	0.13 0.15	- 0 17

Note 1: Other oxygen-containing hydrocarbon compounds include acetic acid and traces of propanol and butanol.

Note 2: Other hydrocarbons consist of C_2-C_4 hydrocarbons. Furthermore, about 0.01 to 0.1 millimole of CO_2.

Example 11

Rhodium chloride trihydrate (2.0 g) was dissolved in 100 ml of water, and the solution was impregnated in 30 g of lanthanum oxide powder (purity 99.9%; a product of Nakarai Chemical Co., Ltd.). The impregnated lanthanum oxide was air-dried, and the resulting powder was molded into pellets having a size of about 6 to 10 mesh by a tableting machine. The pellets were packed into a pressure fixed-bed type reactor (40 in diameter x 500 mm in length; lined with Hastelloy-C). Glass beads having a diameter of 2 to 3 mm were filled on the top and bottom of the catalyst layer. The catalyst was heated at 350°C for 5 hours in a stream of hydrogen at atmospheric pressure, and a pressurized synthesis gas was passed through the catalyst layer under the conditions shown in Table 2, and the conversion and the distribution of the products were examined. The off gas was analyzed by TCD gas-chromatography on an active carbon column (1 m, room temperature), and an Al_2O_3-DMF column (4m, room temperature). The resulting oxygen-containing hydrocarbon compounds were bubbled through two traps containing 200 ml of water, and the absorbed oxygen-containing hydrocarbon compounds were quantitatively and qualitatively analyzed by FID (flame ionization detector) gas-chromatography. The results are shown in Table 2.

Example 12

Rhodium nitrate hydrate ($Rh(NO_3)_3 \cdot xH_2O$) (1.25 g) was dissolved in 100 ml of water, and 20 g of zirconium oxide powder (99.9% pure; a product of Nakarai Chemical Co., Ltd.) was added to the resulting solution to impregnate the powder with the aqueous solution. The impregnated zirconium oxide was dried by a rotary evaporator under reduced pressure, and pelletized by a tableting machine. The resulting pellets were packed into a high-pressure reactor, and reduced in a stream of hydrogen at 250°C and 1 atmosphere. A gaseous mixture consisting of CO and H_2 in a mole ratio of 0.5 or 1.0 was introduced, and reacted at a temperature of 250 to 320°C under a pressure of 10, 20 or 40 atmospheres. The conversion of CO and the distribution of the resulting products are shown in Table 2.

Example 13

Rhodium chloride trihydrate (0.50 g) was deposited on 20 g of zirconium oxide (99.9%; a product of Nakarai Chemical Co., Ltd.) from its aqueous solution in the same way as in Example 1. After drying, the impregnated zirconium oxide was dried and molded into pellets having a size of 8 to 10 mesh. The pellets were packed into a high-pressure fixed bed reactor, and subjected to reducing treatment in a stream of hydrogen (1000 ml/min.) at 350°C and 1 atmosphere for 5 hours. Then the CO-H_2 reaction at an elevated pressure was performed in the reactor under the conditions shown in Table 2. The results are also shown in Table 2.

For comparison, the results obtained by using silica-Rh are also shown in Table 2.

Table 2

Example	Catalyst	Reaction conditions: Pressure (kg/cm^2) Tempera-ture (^oC)	Reaction conditions: CO/H_2 mole ratio	Reaction conditions: Flow rate (ml/min.)	Amounts of the products formed (mmole/hr): CH_3OH	C_2H_5OH	CH_3CHO	CH_3COOH	C_1	Other hydro-carbons (*)	CE (%)
11	La_2O_3-Rh (Rh 0.80 g)	10 K 305 ^oC	0.5	200	0.67	3.22	0.05	0.10	9.1	2.1	35.9
		20 K 310 ^oC	0.5	400	2.93	8.0	0.11	0.35	13.3	0.84	51.0
		40 K 270 ^oC	0.5	800	5.53	12.9	0.43	0.75	21.0	1.05	59.2
12	ZrO_2-Rh (Rh 0.40 g)	20 K 296 ^oC	0.5	800	0.10	1.04	0.48	+	4.14	0.30	38.2
		40 K 336 ^oC	1.0	800	0.02	1.46	0.55	0.62	8.50	1.04	32.5
13	ZrO_2-Rh (Rh 0.20 g)	10 K 275 ^oC	0.5	800	0.75	0.64	0.17	+	3.84	0.23	34.9
		20 K 294 ^oC	0.5	800	0.83	1.27	0.30	+	8.7	0.31	29.7
		40 K 275 ^oC	0.5	800	0.62	0.43	0.16	*	2.40	0.14	39.5
Comparative Example 2	SiO_2-Rh (Rh 0.50 g)	10 K 252 ^oC	0.5	800	0.01	0.076	0.75	0.08	10.1	2.9	8.6
		10 K 294 ^oC	0.5	800	0.08	0.5	1.4	0.10	22.0	9.0	7.3
		20 K 266 ^oC	1.0	800	0.04	0.24	1.4	0.10	9.3	5.6	10.7
		20 K 292 ^oC	1.0	800	0.04	0.91	1.6	0.10	18.2	5.4	12.8

Note: The other hydrocarbons consist of C_2-C_4 hydrocarbons. A small amount of CO_2 formed, but was not included in determining the carbon efficiency in this table.

Example 14

Rhodium chloride trihydrate (1.25 g) and 0.56 g of manganese chloride tetrahydrate were dissolved in 100 ml of distilled water, and 40 g of pellets of zirconium oxide (2 mm in diameter x 2 mm in length, surface area 50 m^2/g; a product of Strem Chemicals Co.Ltd) was added to the aqueous solution. The impregnated zirconium oxide was evaporated to dryness by a rotary evaporator, and packed into a flowing type reactor (made of a Pyrex glass having a size of 18 mm in diameter x 350 mm in length. Glass beads having a diameter of 2 to 3 mm were packed on the top and bottom of the catalyst layer. The catalyst was subjected to reducing treatment in a gaseous mixture at atmospheric pressure of hydrogen and helium (H_2 20 ml/min., He 40 ml/min.) at 350°C for 15 hours. A gaseous mixture of CO and H_2 (diluted with He; total pressure 1 atmosphere) was passed through the catalyst layer, and reacted. The conversion of CO and the distribution of the products were examined. The products were analyzed in the same way as in Example 11. The results are shown in Table 3.

Comparative Examples 3 and 4

For comparison, 1.25 g of rhodium chloride trihydrate was deposited on 40 g of zirconium oxide (surface area 50 m^2/g; a product of Strem Chemicals Co. Ltd.), followed by reduction with hydrogen at 350°C for 15 hours to form a catalyst (A). Separately, an aqueous solution of 1.25 g of rhodium chloride trihydrate and 0.50 g of manganese chloride tetrahydrate was impregnated in silica pellets (10 to 20 mesh, surface area 100 m^2/g; a product of Japan Gasoline Chemical Company), followed by reducing treatment in a hydrogen stream at 350°C for 15 hours, to form a catalyst (B).

The $CO-H_2$ reaction was performed under atmospheric pressure using the same reactor as used in Example 9 in the presence of catalyst (A) or (B). The results are shown in Table 3.

It is seen from a comparison of Example 14 with Comparative Examples 3 and 4 that by using a catalyst comprising zirconium oxide, rhodium and manganese, the selectivity for ethanol and the carbon efficiency of the oxygen-containing hydrocarbon compounds in the $CO-H_2$ reaction increase.

Table 3

Example	Catalyst	Feed gas (1 atm.)			Reaction temperature (°C), one-pass CO conversion (%)
		CO (ml/min.)	H_2 (ml/min.)	He (ml/min.)	
14	Rh-Mn-ZrO_2 (Rh 0.50 g, Mn 0.15 g)	20 20 25	40 40 50	20 20 20	212 °C, 3.5 % 220 °C, 8.0 % 212 °C, 2.9 %
Comparative Example 3	Rh-ZrO_2 (catalyst A) (Rh 0.50 g)	20 20 20	40 40 40	20 20 20	200 °C, 1.7 % 212 °C, 2.6 % 222 °C, 5.3 %
Comparative Example 4	Rh-Mn-SiO_2 (catalyst B) (Rh 0.50 g, Mn 0.14 g)	20 20 20	40 40 40	20 20 20	230 °C, 0.32 % 260 °C, 1.5 % 290 °C, 4.8 %

- to be continued -

Table - 2 (continued)

Example	Amounts of the products (m-moles/hr) (*)									CE (%)	Ethanol selectivity (%)
	CH_3OH	C_2H_5OH	CH_3CHO	CH_3COOH	C_1	C_2	C_3	C_4	CO_2		
14	-	0.382	0.004	±	0.670	0.044	0.070	±	0.057	43	99
	-	0.478	0.01	±	2.13	0.11	0.26	+	0.13	23	98
	-	0.370	0.02	±	0.820	0.034	0.094	±	0.01	40	95
Comparative Example 3	-	0.163	0.03	±	0.374	0.1010	0.057	+	0.01	36	98
	-	0.164	0.05	±	0.676	0.020	0.088	+	0.01	27	97
	-	0.260	0.02	±	1.140	0.047	0.182	0.026	0.036	22	90
Comparative Example 4	-	0.007	0.0015	±	0.130	0.010	±	±	±	10.1	82
	-	0.035	0.014	+	0.348	0.093	0.052	±	+	12.4	72
	-	0.031	0.032	0.001	1.27	0.28	0.166	±	0.052	5.0	48

Note: Acetic acid was obtained as ethyl acetate. The ethyl groups of diethyl ether formed as by-product and ethyl acetate were included in the amount of ethanol formed.

Examples 15 to 18

Rhodium chloride trihydrate (1.25 g) and 0.5 to 0.6 g of rhenium chloride, niobium chloride, tantalum chloride or chromium chloride were dissolved in methanol, or ethanol. The resulting solution was impregnated in pellets of zirconium oxide (2 mm in diameter x 2 mm, surface area 50 m^2/g; a product of Strem Chemicals Co. Ltd.). The solvent was then removed by drying under reduced pressure, and the impregnated zirconium oxide pellets were subjected to reducing treatment in a gaseous mixture of H_2 (20 ml/min.) and He (40 ml/min.) at 350°C for 15 hours to prepare a catalyst. Using the resulting catalyst, the $CO-H_2$ reaction was carried out at atmospheric pressure by the same operation as in Example 14. The conversion of CO and the distribution of the products were examined, and are shown in Table 4.

Table 4

Example	Catalyst	Feed composition (1 atm.) CO (ml/min.)	H_2 (ml/min.)	He (ml/min.)	Reaction temperature (°C), one-pass CO conversion (%)	
15	Rh-Re-ZrO_2 (Rh 0.50 g, Re 0.26 g)	20	40	20	182°C,	1.7 %
		20	40	20	193°C,	3.8 %
		40	40	0	205°C,	2.5 %
16	Rh-Nb-ZrO_2 (Rh 0.50 g, Nb 0.19 g)	20	40	20	162°C,	1.4 %
		20	40	20	175°C,	2.8 %
		20	40	20	188°C,	8.0 %
17	Rh-Ta-ZrO_2 (Rh 0.50 g, Ta 0.27 g)	20	40	20	180°C,	1.2 %
		20	40	20	195°C,	5.5 %
		20	40	20	210°C,	7.6 %
18	Rh-Cr-ZrO_2 (Rh 0.50 g, Cr 0.20 g)	20	40	20	200°C,	2.3 %
		20	40	20	220°C,	5.7 %
		40	40	0	200°C,	1.4 %

- to continued -

Table - 4 - (continued)

Example	Amounts of the products (mmoles/hr) (*)									CE (%)	Ethanol selectivity (%)
	CH_3OH	C_2H_5OH	CH_2CHO	CH_3COOH	C_1	C_2	C_3	C_4	CO_2		
15	-	0.293	±	±	0.249	0.004	0.009	+	0.005	67	99.9
	-	0.509	0.002	-	0.696	0.042	0.046	+	0.016	52	99
	-	0.610	0.003	-	1.000	0.050	0.07	0.007	0.007	48	99
16	-	0.250	0.030	±	0.130	+	0.020	±	±	76	89
	-	0.435	0.046	±	0.473	0.009	0.010	0.002	±	65	90
	-	0.804	0.080	±	1.300	0.042	0.220	0.090	±	42.4	90
17	-	0.158	0.027	0.024	0.198	0.003	0.005	±	±	65.6	75.5
	-	0.394	0.055	0.046	0.700	0.078	0.276	0.052	0.003	34.3	79.6
	-	0.526	0.064	0.059	1.510	0.042	0.310	0.042	0.004	32.4	81
18	-	0.240	0.011	+	0.520	0.003	0.057	+	-	41.8	96
	-	0.370	0.017	+	1.660	0.036	0.160	+	-	26.0	96
	-	0.260	0.034	+	0.367	0.0002	0.0005	±	-	61.3	38

Note: Acetic acid was obtained as ethyl acetate. The ethyl groups of diethyl ether formed as by-product and ethyl acetate were included in the amount of ethanol.

Example 19

Thirty grams of zirconium oxide (a product of Nakarai Chemical CO., Ltd; 99.9%, surface area 30 m^2/g) was dissolved in a solution of 0.90 g of rhodium chloride trihydrate and 0.40 g of rhenium chloride in 100 ml of methanol. The solvent was removed by drying under reduced pressure in a rotary evaporator to afford a reddish brown powder. The powder was pelletized by a tableting machine under a pressure of 350 kg/cm^2 to form pellets having a size of 10 to 20 mesh. The pelletized catalyst was packed into a flow-type reactor, and subjected to reducing treatment in a stream of hydrogen at 350°C for 15 hours. Then, the CO-H_2 reaction was performed under atmospheric pressure. The results are shown in Table 5.

Example 20

Rhodium chloride trihydrate (1.25 g) and 0.50 g of manganese nitrate hexahydrate (a product of Wako Pure Chemical Co., Ltd.; 99% pure) were dissolved in 100 ml of water, and 40 g of pellets of zirconium oxide (2 mm in diameter x 2 mm; a product of Strem Chemicals Co.Ltd) was impregnated with the aqueous solution. The impregnated zirconium oxide pellets were dried by evaporation in a rotary evaporator, and packed into a flow-type reactor made of a Pyrex glass, and subjected to reducing treatment in a stream of hydrogen (a mixture of H_2 (20 ml/min.) and He (40 ml/min.)) at 350°C for 15 hours. A gaseous mixture of CO and H_2 was passed through the catalyst layer, and the reaction was started under the conditions shown in Table 5. The conversion of CO and the amounts of the products yielded per hour were examined, and the results are shown in Table 5.

Table 5

	Example 19			Example 20	
Catalyst	Rh-Re-ZrO_2 (Rh 0.36 g, Re 0.20 g)			Rh-Mn-ZrO_2 (Rh 0.50 g, Mn 0.10 g)	
Feed composition (ml/min. at 1 atm.)					
CO	20	20	20	20	20
H_2	40	40	40	40	40
He	20	20	20	20	20
Reaction temperature (°C), One-pass CO conversion (%)	200°C 2.6 %	225°C 3.5 %	185°C 0.8 %	200°C 3.2 %	215°C 7.4 %
Amounts of the products (mmole/hr) (*)					
CH_3OH	0.006	0.007	±	-	-
C_2H_5OH	0.318	0.308	0.151	0.375	0.485
CH_3CHO	0.006	0.010	±	0.005	0.020
CH_3COOH	±	±	±	±	±
C_1	0.478	0.707	0.123	0.598	1.95
C_2	0.036	0.109	0.002	0.032	0.12
C_3	0.028	0.073	0.004	0.065	0.15
C_4	±	±	±	±	0.02
CO_2	0.060	0.062	0.002	0.047	0.12
CE (%)	48.9	35.3	68.3	45.6	26.3
Ethanol selectivity (%)	97.5	95	99	98	96

Note: Acetic acid was obtained as methanol and ethyl acetate. The ethyl groups of by-product diethyl ether and ethyl acetate were included in the amount of ethanol.

Example 21

A gaseous mixture of CO, CO_2 and H_2 was passed through the catalyst prepared in Example 16, and reacted under the conditions shown in Table 6. The amounts of the products yielded per hour are shown in Table 6.

Table 6

	Example 21	
Catalyst	Rh-Nb-ZrO_2 (Rh 0.50 g, Nb 0.19 g)	
Reaction temperature (°C)	175	182
Feed composition (ml/min.)		
CO	15	20
H_2	40	40
He	20	20
CO_2	5	5
Amounts of the products (m-moles/hr)		
CH_3OH	-	-
CH_3CHO	0.05	0.05
C_2H_5OH	0.38	0.57
Diethyl ether	0.02	0.03
CH_3COOH	0.01	0.01
C_1	0.46	0.81
C_2	0.01	0.04
C_3	0.02	0.03
C_4	±	0.01

Example 22

Rhodium chloride trihydrate (1.25 g) and 0.50 g of rhenium chloride were dissolved in 100 ml of methanol. The resulting solution was impregnated in titanium oxide pellets (a product of Ishihara Sangyo K.K.; in the form of balls with a diameter of 2 to 3 mm, surface area 40 m^2/g). The impregnated titanium oxide pellets were dried under reduced pressure, and subjected to reducing treatment at 350°C for 15 hours in a gaseous mixture consisting of H_2 (20 ml/min.) and He (40 ml/min.) to prepare a catalyst. Using the resulting catalyst, the CO-H_2 reaction was carried out under atmospheric pressure by the same operation as in Example 14. The results are shown in Table 7.

Examples 23 and 24

Rhodium chloride trihydrate (1.25 g) and 0.50 g of rhenium chloride were deposited from their methanol (100 ml) solution on 30 g of each of lanthanum oxide powder and thorium oxide (RG; a product of Kishida Chemical Co., Ltd.) by the same operation as in Example 22. The resulting supported product was pelletized by a tableting machine, and packed into a reactor. It was subjected to the same hydrogen reducing treatment as in Example 22 and then, the CO-H_2 reaction was performed using the resulting catalysts. The results are shown in Table 7.

Table 7

	Example 22		Example 23		Example 24	
Catalyst	$Rh-Re-TiO_2$ (Rh 0.50 g, Re 0.26 g)		$Rh-Re-La_2O_3$ (Rh 0.50 g, Re 0.26 g)		$Rh-Re-ThO_2$ (Rh 0.50 g, Re 0.26 g)	
Feed composition (ml/min. at 1 atm.)						
CO	20	20	20	20	20	20
H_2	40	40	40	40	40	40
He	20	20	20	20	20	20
Reaction temperature (°C), One-pass CO conversion (%)	185°C 1.78%	205°C 5.6 %	200°C 1.7 %	215°C 3.6 %	180°C 2.9 %	205°C 5,1 %
Amounts of the products (mmoles/hr)						
CH_3OH	+	+	0.175	0.205	0.032	0.015
C_2H_5OH	0.211	0.581	0.152	0.310	0.286	0.459
CH_3CHO	0.023	0.036	0.020	0.032	+	0.014
CH_3COOH	+	+	+	+	+	+
C_1	0.380	1.315	0.320	0.595	0.489	0.721
C_2	0.013	0.046	0.004	0.028	0.058	0.135
C_3	0.018	0.066	0.008	0.022	0.089	0.170
C_4	0.006	0.012	0.001	0.002	0.004	0.018
CO_2	0.012	0.019	0.038	0.281	0.055	0.130
CE (%)	49	42	57	47	40	35
Ethanol selectivity (%)	90	94	58	70	95	96

Example 25

Zirconium oxynitrate dihydrate (2.5 g) was dissolved in 100 ml of distilled water, and 10 g of silica gel pellets (8 - 10 mesh; a product of Fuji-Davison Chemical Ltd., # 57) were added. After dipping, the silica gel pellets were dried by a rotary evaporator, and heat-treated at 500°C for 15 hours in an electric furnace to decompose zirconium oxynitrate to zirconium oxide (decomposition temperature 230°C) to obtained zirconium oxide-supported silica gel pellets. Rhodium chloride trihydrate (1.2 g) was dissolved in 100 ml of methanol to form a crimson solution. The zirconium oxide-supported silica pellets were added to the solution, and after dipping, the methanol was evaporated off by a rotary evaporator to obtain a rhodium chloride-supported product. Ten gram of the rhodium chloride-supported product was packed into a flowing-type reactor of Pyrex glass (18 mm in diameter x 500 mm in length). Glass beads were placed on the top and bottom of the catalyst layer. While passing a hydrogen gas (1 atmosphere), the temperature was gradually raised from room temperature. Then, the $CO-H_2$ reaction was performed at a total pressure of 1 atmosphere by passing a gaseous mixture of CO and H_2 diluted with He ($CO:H_2:He$=20:40:20 ml/min.) through the catalyst layer. At about 150 to 250°C, the amounts of oxygen-containing hydrogen compounds and hydrocarbons formed were measured.

The resulting oxygen-containing hydrocarbon compounds consisted of ethanol as a main ingredient, methanol, acetaldehyde, acetic esters, and traces of propanol and butanol. Every one hour, the off gas was bubbled through 50 ml of distilled water (condenser), and the resulting oxygen-containing hydrocarbon compounds were absorbed and trapped. The products were qualitatively and quantitatively analyzed by an FID gas chromatographic analyzer (Shimazu 7A) using a Porapak Q column (4 m, 200°C, N_2 gas carrier). For calibration, acetone was used as an internal standard. Methane, CO_2 and CO were analyzed by an active carbon column (1 m, room temperature). C_2-C_4 hydrocarbons were analyzed qualitatively and quantitatively by a TCD gas chromatographic analyzer (Shimazu 4B) using an alumina-dimethylformamide (supported in an amount of 38% by weight) column. As a result of the overall analysis of the products shown in Table 8, the performance of the present catalyst in the CO-H_2 reaction at atmospheric pressure was shown by the conversion of CO, the carbon efficiency (or selectivity) of oxygen-containing hydrocarbon compounds based on the converted CO and the selectivity for ethanol in the oxygen-containing hydrocarbon compounds.

Example 26

Rhodium chloride was deposited from its methanol solution on 10 g of silica gel (Davison # 57), and the supported product was subjected to reducing treatment in a hydrogen stream (H_2:He=40:40, ml/min.) at 1 atmosphere. A solution of 25 g of zirconium oxynitrate dihydrate in 100 ml of methanol was added to the resulting rhodium-silica catalyst. The impregnated catalyst was evaporated in a rotary evaporator to remove the solvent. The resulting catalyst was again packed into a flowing-type reactor, and subjected to reducing treatment in a stream of hydrogen at 400°C and 1 atmosphere. Using the resulting rhodium-zirconia-silica catalyst the CO-H_2 reaction was carried out at atmospheric pressure in the same way as in Example 22. The results are shown in Table 8.

Example 27

A mixture of 1.2 g of rhodium chloride trihydrate and 2.5 g of zirconium oxynitrate dihydrate was dissolved in 100 ml of methanol, and 10 g of silica gel (Davison #57) was added to the solution. The impregnated silica gel was dried in a rotary evaporator to remove the methanol. The product was subjected to reducing treatment in hydrogen in the same way as in Example 25 to prepare a rhodium-zirconia-silica catalyst. Using 10 g of the resulting catalyst, the CO-H_2 reaction was performed at atmospheric pressure. The results are shown in Table 8.

Comparative Example 5

For comparison, a rhodium-silica catalyst was prepared by the same operation as in Example 25 except that 1.2 g of rhodium chloride trihydrate was deposited on 10 g of silica gel (Davison #57) from its methanol solution. Using 10 g of the resulting catalyst, the CO-H_2 reaction was carried out under atmospheric pressure in the same way as in Example 25. The results are shown in Table 8.

It is seen from the results given in Table 8 that the silica-supported rhodium catalyst containing zirconium oxide gives a much higher CO conversion and a much higher selectivity for oxygen-containing hydrocarbon compounds, especially ethanol, than does the silica-supported rhodium catalyst not containing zirconium oxide.

Table 8

	Example 25		Comparative Example 5			Example 26	Example 27
Catalyst	$Rh/ZrO_2/SiO_2$ (Rh 0.48 g) ZrO_2/SiO_2=11.4 wt%		Rh/SiO_2 (Rh 0.48 g)			Rh/SiO_2-ZrO_2 (Rh 0.48 g) ZrO_2/SiO_2=11.4 wt%	$Rh-ZrO_2-SiO_2$ (Rh 0.48 g) ZrO_2/SiO_2=11.4 wt%
Reaction conditions							
SV (H^{-1})	192	192	192	192	192	192	192
Temperature (°C)	200	216	264	278	245	200	200
CO/H_2 mole ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed (ml/min.)	80	80	80	80	80	80	80
Amounts of the products (mmoles/hr)							
CH_3OH	0.09	0.04	-	-	0.01	0.026	-
CH_3CHO	0.042	0.074	0.027	0.008	0.029	0.026	0.047
C_2H_5CH	0.363	0.470	-	0.003	0.010	0.351	0.725
CH_2COCH	-	0.033	-	-	-	-	0.001
C_1	0.47	1.45	1.18	2.67	0.47	0.68	1.74
C_2	0.02	0.061	0.08	0.14	0.02	0.031	0.050
C_3	0.004	0.213	0.02	0.023	0.004	0.155	0.156
C_4	-	-	-	-	-	-	0.045
CC_2	-	0.011	0.03	0.03	-	0.042	0.024
CO conversion (mole %)	3.7	6.6	3.3	7.3	1.4	3.93	7.97
CE (%)	47.3	46.4	3.7	0.8	14.9	38.5	38.5
Ethanol selectivity (%)	80.8	78.7	-	27	22	90.0	93.8
STY (g/kg cat. hr^{-1})	2.1	2.8	0.12	0.05	0.17	1.8	3.5

Example 28

Zirconium oxynitrate dihydrate (2.5 g) and 0.9 g (A), 0.6 g (B) or 0.3 g (C) of rhodium chloride trihydrate were added to methanol. Ten grams of silica gel (Davison # 57) was added to the resulting methanol solution. After sufficient dipping, the silica gel was dried by a rotary evaporator to remove the methanol. Each of the resulting products was packed in a flowing-type reactor and subjected to reducing treatment at 400°C for 15 hours in a hydrogen stream at 1 atmosphere by the same operation as in Example 25. Using each of the catalysts obtained after the reducing treatment, a gaseous mixture of CO and H_2 diluted with He was reacted under atmospheric pressure. The reaction products obtained in the steady state at predetermined temperatures were analyzed, and the results are shown in Table 9.

Table 9

Catalyst	Example 28 A		B	C
	Rh-ZrO_2/SiO_2 (Rh 0.36 g) ZrO_2/SiO_2 = 11.4 wt%		Rh-ZrO_2/SiO_2 (Rh 0.24 g) ZrO_2/SiO_2 = 11.4 wt%	Rh-ZrO_2/SiO_2 (Rh 0.12 g) ZrO_2/SiO_2 = 11.4 wt%
Reaction conditions				
SV (hr^{-1})	192	192	192	192
Temperature(°C)	200	190	201	200
CO/H_2 mole ratio	0.5	0.5	0.5	0.5
Feed (ml/min.)	80	80	80	80
Amounts of the products (mmoles/hr)				
CH_3OH	0.030	-	0.023	0.020
CH_3CHO	0.048	0.031	0.025	0.019
C_2H_5OH	0.521	0.270	0.249	0.099
CH_3COOH	0.019	0.001	-	-
C_1	1.18	0.510	0.536	0.295
C_2	0.032	0.019	0.016	0.013
C_3	0.118	0.068	0.061	0.046
C_4	0.023	trace	-	-
CO_4	0.086	trace	-	trace
CO conversion	5.6	2.7	2.6	1.4
CE (%)	42.8	45.0	43.3	35.8
Ethanol selectivity (%)	86.4	87.5	87.2	77.3
STY (g/kg catalyst hr-1)	2.7	1.4	1.3	0.60

Example 29

Zirconium tetra-n-propoxide (6.24 g) was dissolved in 100 ml of n-hexane, and 20 g of silica gel (8-10 mesh; Davison #57) was dipped in the solution. The n-hexane was then evaporated by a rotary evaporator, and the dried product was fired in the air in an electric furnace at 200°C for 1.5 hours and then at 500°C for 16 hours to form ZrO_2. Ten grams of the resulting zirconium oxide-supported silica pellets were dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol. The impregnated pellets were dried by a rotary evaporator to remove the solvent to obtain a rhodium chloride catalyst precursor. Ten grams of the catalyst precursor was packed into the same apparatus as used in Example 25, and heat-treated in a stream of hydrogen at 100°C for 1.5 hours, and then at 400°C overnight. Using the resulting catalyst, the same $CO-H_2$ reaction as in Example 25 was carried out. The results are shown in Table 10.

Example 30

Dicyclopentadienyl zirconium dichloride (2.7 g) was dissolved in 100 ml of tetrahydrofuran, and 10 g of silica gel (8-10 mesh, Davison #57) and dipped in the solution. During the dipping, the solution was refluxed over a warm bath. Then, the impregnated silica gel was dried to remove the tetrahydrofuran. A solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol was added to the dried product to deposit rhodium chloride thereon. The solvent was evaporated off to dry the supported catalyst precursor. Ten grams of the catalyst precursor was packed into the same apparatus as used in Example 25, and subjected to reducing treatment in hydrogen stream first at 200°C for 1 hour and then at 395°C overnight. Using the resulting catalyst, the $CO-H_2$ reaction was performed in the same way as in Example 25. The results are shown in Table 10.

Example 31

Rhodium chloride trihydrate (0.6 g) and 2.5 g of zirconium oxynitrate dihydrate were dissolved in 40 ml of methanol. Ten grams of a silica carrier (a product of Japan Gasoline Chemical Co., Ltd.; surface area 100 m^2/g) was dipped in the solution. The impregnated silica carrier was dried to evaporate the solvent. Five grams of the dried product was packed into the same apparatus as used in Example 17, and heat-treated in a stream of nitrogen at 400°C overnight to decompose and reduce the nitrate. Using the resulting catalyst, the same reaction as in Example 25 was carried out. The results are shown in Table 10.

Example 32

Titanium tetraisopropoxide (5.5 g) was dissolved in 100 ml of n-hexane, and 20 g of silica gel (Davison #57) was dipped in the solution. The solvent was evaporated off, and the impregnated silica gel was heat-treated in the air in a drying furnace first at 200°C for 1.5 hours and then at 500°C overnight. Ten grams of the TiO_2-SiO_2 carrier was dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol to deposit rhodium chloride. The resulting product was dried by a rotary evaporator to remove the methanol, and then heat-treated overnight in the same apparatus as used in Example 25 in a stream of hydrogen at 350°C. The results obtained are shown in Table 10.

Table 10

Catalyst	Example 29 Rh/ZrO_2-SiO_2 (Rh 0.48 g) ZrO_2/SiO_2=23.5 wt%			Example 30 Rh/ZrO_2-SiO_2 (Rh 0.48 g) ZrO_2/SiO_2=11.4 wt%		Example 31 Rh-ZrO_2/SiO_2 (Rh 0.24 g) ZrO_2/SiO_2=22.8 wt%		Example 32 Rh/TiO_2-SiO_2 (Rh 0.48 g) TiO_2/SiO_2=15.7 wt%	
Reaction conditions									
SV (h^{-1})	200	490	1025	190	190	200	200	190	190
Temperature (°C)	194	194	197	194	190	191	189	181	186
CO/H_2 mole ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed (ml/min.)	8.3	204	427	79	79	42	42	79	79
Amounts of the products (mmoles/hr)									
CH_3OH	0.023	0.032	0.071	0.012	0.010	0.017	0.011	0.057	0.037
CH_3CHO	0.050	0.050	0.065	0.070	0.051	0.025	0.016	0.075	0.093
C_2H_5OH	0.835	1.055	1.257	1.064	0.853	0.326	0.281	0.710	0.909
CH_3COOH	grace	trace	trace	trace	trace	trace	trace	trace	trace
C_1	1.198	1.260	1.304	1.685	1.232	0.815	0.348	1.151	2.16
C_2	0.067	0.052	0.067	0.121	0.094	0.029	0.024	0.033	0.063
C_3	0.224	0.204	0.284	0,373	0.294	0.087	0.080	0.158	0.283
C_4	0.079	0.107	0.106	0.139	0.161	0.090	0.048	0.094	0.153
CO_2	0.070	0.047	0.047	0.080	0.061	0.059	0.039	0.070	0.124
CO Conversion (%)	7.8	3.5	2.0	11.0	9.0	4.54	3.0	7.7	10.2
CE (%)	43	48	49	38	86	52	41	47.4	39.7
Ethanol selectivity (%)	93	94	93	93	94	91	93	81	85
STY (g/kg catalyst h^{-1})	4.1	5.2	6.2	5.2	4.2	3.3	2.8	3.8	4.7

Example 33

Ten grams (25 ml) of the catalyst used in Example 25 was packed in a stainless steel pressure reactor (lined with titanium metal and having a size of 40 mm in diameter and 500 mm in length), and subjected to reducing treatment in a stream of hydrogen under 1 atmosphere at 350°C for 5 hours. Then, a gaseous mixture of CO and H_2 under pressure was passed through the catalyst layer. The products at the exit of the reactor were analyzed, and the results are shown in Table 11.

Oxygen-containing hydrocarbon compounds were trapped by bubbling the off gas through two series-connected absorbing towers containing 200 ml of distilled water, and the trapped liquor was quantitatively analyzed by an FIF gas-chromatographic analyzer (steam gas-chromatographic analyzer including a cerite column; a product of Okura Rika K.K.) every predetermined period of time. C_1-C_4 hydrocarbons, CO and CO_2 in the off gas were analyzed by a TCD gas-chromatographic analyzer using both an active carbon column (1 m, room temperature, and an Al_2O_3-DMF (supported in an amount of 38% by weight) column (4 m, room temperature).

Comparative Example 6

For comparison, the activity of a catalyst prepared by depositing rhodium chloride trihydrate on silica and subjecting the product to reducing treatment in hydrogen at 350°C was examined in the reaction of a synthesis gas at low to medium pressures. The results are also shown in Table 11.

Table 11

Catalyst	Example 33: Rh/ZrO_2-SiO_2 (Rh 0.48 g, ZrO_2/SiO_2 = 11.4 wt%)						Comparative Example 6: Rh/SiO_2 (Rh 0.48 g)	
CO Conversion (mole %)	1.1	2.2	2.4	1.5	1.7	1.5	3.7	1.1
Reaction conditions								
Gas pressure (kg/cm^2)	20	20	20	20	40	40	20	20
Temperature (°C)	240	240	220	220	240	240	292	282
CO/H_2 mole ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed (ml/min.)	2400	800	800	1600	1600	2400	800	800
SV (h^{-1})	5760	1920	1920	3840	3840	5760	960	960
Amounts of the products (mmoles/hr)								
CH_3OH	2.75	0.85	1.23	2.51	3.16	4.42	0.04	0.04
CH_3CHO	0.58	0.36	0.47	0.57	0.78	1.20	1.59	0.87
C_2H_5OH	5.32	3.08	3.42	5.07	5.11	7.00	0.91	0.24
CH_3COOH	1.00	1.20	1.41	1.26	1.67	2.53	trace	trace
C_3H_7OH	trace	trace	trace	trace	trace	trace	trace	trace
C_4H_9OH	trace	trace	trace	trace	trace	trace	trace	trace
C_1	3.23	3.47	3.13	2.82	3.25	3.80	18.2	3.67
C_2	0.085	0.083	0.110	0.117	0.099	0.067	2.70	0.89
C_3	0.128	0.114	0.106	0.114	0.116	0.114	2.69	1.92
C_4	trace	trace	trace	trace	trace	trace	0.12	1.04
CO_2	0.115	trace	0.060	0.117	0.119	0.269	-	-
CE (%)	80.7	71.2	76.0	82.2	82.3	84.9	11.2	12.8
STY (g/kg of catalyst hr^{-1})	42.1	26.6	30.4	41.6	47.3	67.4	11.5	5.2

Example 34

Using 10 g of the catalyst (Rh/ZrO_2-SiO_2) prepared in Example 25, a gaseous mixture of CO, CO_2 and H_2 under a total pressure of 1 atmosphere was reacted. The amounts of the products formed per hour are shown in Table 12.

Table 12

Catalyst	Rh/ZrO_2-SiO_2	
Temperature (^oC)	200	200
Feed composition (ml/min.)		
CO	20	15
H_2	40	40
He	20	20
CO_2	5	5
Amounts of the products (mmole/hr)		
CH_3OH	0.08	0.07
CH_3CHO	0.041	0.038
C_2H_5OH	0.361	0.340
CH_3COOH	trace	trace
C_1	0.48	0.30
C_2	0.02	0.02
C_3	0.04	0.03
C_4	trace	trace
CE (%)	58.0	61.8

Example 35 and Comparative Example 7

Thorium acetylacetonate (12 g) was dissolved in 200 ml of benzene, and 20 g of silica gel (Davison #57) heat-treated in vacuum at 300°C for 3 hours was dipped in the solution by standing overnight at room temperature. The solvent was evaporated off by using a rotary evaporator, and the dried product was heated in the air first at 200°C for 2 hours and then at 500°C for 24 hours to obtain thorium oxide-supported silica gel.

Ten grams of the thorium oxide-supported silica gel was dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol. The methanol was evaporated off to obtain a rhodium-supported catalyst. Ten grams of the catalyst was packed into a flow-type reactor of Pyrex glass (20 mm in diameter and 450 mm in length), and subjected to reducing treatment in hydrogen at 400°C overnight after gradually raising the temperature from room temperature.

A gaseous mixture of CO and H_2 diluted with He was passed under a total pressure of 1 atmosphere through the resulting catalyst layer, and reacted. The CO:H_2:He mole ratio of the gaseous mixture was 1:2:1, and the reaction temperature was varied between 180 and 250°C. The reaction products were quantitatively and qualitatively analyzed in the same way as in Example 25. The results are shown in Table 13.

For comparison, a catalyst was prepared in the same way as in Example 35 except that 1.2 g of rhodium chloride trihydrate was deposited on 10 g of silica gel (Davison #57) from its methanol solution. Using 10 g of the resulting catalyst, the CO-H_2 reaction was carried out under atmospheric pressure, and the results are shown in Table 13.

Example 36

Thorium nitrate tetrahydrate (8.05 g) was dissolved in 100 ml of distilled water, and 15 g of silica gel (Davison #57) heat-treated in vacuum at

300°C for 2 hours was dipped in the solution. The solvent was evaporated off by a rotary evaporator, and the dried product was heated overnight at 500°C in an electric furnace. Ten grams of the resulting thorium oxide-supported silica gel was dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol. The methanol was evaporated off. Ten grams of the resulting catalyst was packed into the same apparatus as in Example 35, and subjected to reducing treatment in a stream of hydrogen at 370°C overnight after raising the temperature from room temperature. Using the resulting catalyst, the same reaction as in Example 35 was carried out. The results are shown in Table 13.

Table 13

Example	Catalyst	Reaction conditions: Feed composition (ml/min.) H_2	CO	He	SV (hr^{-1})	Temperature (°C.)
35	Rh-ThO_2-SiO_2 (Rh 0.48 g) ThO_2/SiO_2=25 wt%	40 40 40 200	20 20 20 100	20 20 20 100	200 200 200 1000	199 190 221 224
36	Rh-ThO_2-SiO_2 (Rh 0.48 g) ThO_2/SiO_2=26 wt%	41.7 40 200	20.0 20 100	19.5 20 100	200 200 1000	200 217 217
Comparative Example 7	Rh-SiO_2 (Rh 0.48 g)	40 40 40	20 20 20	20 20 20	192 192 192	264 278 245

- to be continued -

Table 13 - (continued)

Example	Composition of the product: Oxygen-containing hydrocarbon compounds (mmoles/hr)						Hydrocarbons (mmoles/hour)				
	CH_3CH	C_2H_5OH	CH_3CHO	CH_3COOCH_3	$CH_3COOC_2H_5$	n-C_3H_7OH	C_1	C_2	C_3	C_4	CO_2
35	0.023	0.842	0.025	-	-		0.955	0.045	0.116	0.056	0.031
	0.009	0.383	0.023		0.024	-	0.332	0.018	0.048	0.018	0.065
	0.015	0.783	0.076	-	0.065	0.011	2.445	0.127	0.263	0.121	0.170
	0.020	1.131	0.078	-	0.021	0.031	3.33	0.15	0.317	0.137	0.071
36	0.013	0.289	0.019	-	-	-	0.436	0.032	0.043	0,009	0.082
	0.016	0.232	0.032	-	-	-	0.863	0.061	0.068	0.016	0.095
	0.015	0.318	0.045	-	-	-	0.841	0.048	0.057	-	0.065
Comparative Example 7	-	-	0.027	-	-	-	1.18	0.08	0.02	-	0.03
	-	0.003	0.008	-	-	-	2.67	0.14	0.023	-	0.03
	0.01	0.010	0.029	-	-	-	0.47	0.02	0.004	-	-

- to be continued -

Table - 13 (continued)

Example	CO conversion (mole %)	CE (%)	Ethanol selectivity (%)
35	6.8 3.0 11.9 29	50.8 58.6 32.8 33.5	95.8 88.8 83.7 88.1
36	2.6 3.5 0.67	45.7 28.8 38.3	91.9 85.3 85.8
Comparative Example 7	3.3 7.3 1.4	3.7 0.8 14.9	- 1 27 22

Example 37

Twenty grams of silica gel (Davison #57) heat-treated in vacuum at 300°C for 3 hours was dipped in a solution of 5.5 g of vanadyl tritertiary butoxide ($VO(O\text{-tert-}C_4H_9)_3$) in 100 ml of n-hexane. The solvent was evaporated off, and the dried product was heated in the air in an electric furnace at 200°C for 1.5 hours and at 500°C for a day and night to obtain red vanadium oxide-supported silica gel. Ten gram of the resulting silica carrier was added to a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol to support rhodium chloride. The methanol was evaporated off, and 10 g of the resulting product was subjected to reducing treatment in the same apparatus and by the same method as in Example 35 at 310°C. Using the resulting catalyst, the same reaction as in Example 35 was carried out. The results are shown in Table 14.

Example 38

Twenty grams of silica gel (Davison #57) heat-treated in vacuum at 300°C for 2 hours was dipped in a solution of 10.42 g of tantalum penta-n-butoxide ($Ta(O\text{-n-}C_4H_9)_5$) in 120 ml of n-hexane. The n-hexane was evaporated off, and the dried product was heat-treated in an electric furnace at 200°C for 1 hour, and then at 500°C overnight to obtain tantalum oxide-supported silica gel.

Ten grams of the tantalum oxide-supported silica gel was dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol to deposit rhodium chloride. The methanol was evaporated off, and 10 g of the dried product was subjected to reducing treatment in the same way as in Example 35. Using the resulting catalyst, the same reaction as in Example 35 was carried out. The results are shown in Table 14.

Example 39

Twenty grams of silica gel (Davison #57) heat-treated in vacuum at 300°C for 2 hours was added to a solution of 8.60 g of niobium penta-n-butoxide ($Nb(O\text{-}n\text{-}C_4H_9)_5$) in 100 ml of n-hexane. The n-hexane was evaporated off, and the dried product was heat-treated in an electric furnace at 200°C for 1 hour and then at 500°C overnight. Ten grams of the resulting niobium oxide-supported silica gel was added to a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol to support rhodium chloride. The product was subjected to reducing treatment in the same way as in Example 35. Using the resulting catalyst, the same reaction as in Example 35 was carried out. The results are shown in Table 14.

Example 40

Five grams of vanadyl acetylacetonate ($VO(C_5H_7O_2)_2$) was dissolved in 200 ml of benzene, and 20 g of silica gel (Davison #57) heat-treated in vacuum at 280°C for 3 hours was added to the solution. The benzene was evaporated off, and the dried product was heated in the air in an electric furnace first at 200°C for 2 hours and then at 500°C overnight to obtain vanadium oxide-supported silica gel. Ten grams of the vanadium oxide-supported silica gel was dipped in a solution of 1.2 g of rhodium chloride trihydrate in 100 ml of methanol. The methanol was evaporated off, and 10 g of the dried product was packed into the same apparatus as in Example 35, and subjected to reducing treatment in a stream of hydrogen at 120°C for 1 hour, and after gradually raising the temperature, at 360°C overnight. Using the resulting catalyst, the same reaction as in Example 35 was carried out. The results are shown in Table 14.

Table 14

Example	Reaction conditions					
	Catalyst	Feed composition (ml/min.)			SV	Temperature
		H_2	CO	HO	(hr^{-1})	(°C)
37	Rh-V_2O_5-SiO_2 (Rh 0.48 g) V_2O_5/SiO_2=8.8 wt%	40 200 40	20 100 20	20 100 20	200 1000 200	197 199 183
38	Rh-Ta_2O_5-SiO_2 (Rh 0.48 g) Ta_2O_5/SiO_2=21 wt%	40 40 40 100	20 20 20 50	20 20 20 50	200 200 200 500	196 189 178 194
39	Rh-Nb_2O_5-SiO_2 (Rh 0.48 g) Nb_2O_5/SiO_2=12 wt%	40 40	20 20	20 20	200 200	200 187
40	Rh-V_2O_5-SiO_2 (Rh 0.48 g) V_2O_5/SiO_2=8.6 wt%	40 200	20 100	20 100	200 1000	199 202

- to be continued -

Table 14 - (continued)

Example	Composition of the product										
	Oxygen-containing hydrocarbon compounds (mmoles/hr)						Hydrocarbons (mmoles/hr)				
	CH_3CH	C_2H_5OH	CH_3CHO	CH_3COOCH_3	$CH_3COOC_2H_5$	$n-C_3H_7OH$	C_1	C_2	C_3	C_4	CO_2
37	0.080 0.079 0.025	0.537 0.666 0.300	0.033 0.045 0.018	- - -	0.015 trace 0.006	0.013 0.019 0.005	0.964 1.10 0.352	0.187 0.226 0.061	0.164 0.244 0.075	0.112 0.139 0.022	0.34 0.49 0.31
38	0.126 0.054 0.034 0.049	0.864 0.680 0.497 0.902	0.067 0.051 0.035 0.077	0.011 0.007 0.004 0.003	0.070 0.087 0.063 0.068	- - - 0.025	2.02 1.157 0.572 1.029	0.137 0.082 0.025 0.061	0.511 0.307 0.145 0.233	0.278 0.161 0.085 0.082	0.120 0.097 0.025 0.053
39	0.005 -	0.441 0.232	0.102 0.062	- -	0.087 0.049	0.025 0.003	1.414 0.432	0.243 0.090	0.459 0.179	0.162 0.110	0.533 0.236
40	0.039 0.046	0.347 0.421	0.027 0.029	- -	0.014 -	0.021 0.023	0.662 0.826	0.179 0.201	0.185 0.234	0.123 0.116	0.320 0.272

- to be continued -

Table - 14 (continud)

Example	CO conversion (mole %)	CE (%)	Ethanol selectivity (%)
37	7.5 1.7 3.3	34.3 31.8 38.9	84.2 85.5 87.4
38	13.4 8.8 5.3 3.4	31.3 38.7 48.9 51.5	81.2 81.4 82.2 82.1
39	11.2 4.9	25.4 30.2	69.7 71.1
40	5.7 1.4	30.5 28.2	79.6 80.6

Example 41

A flowing-type pressure reactor made of stainless steel and lined with titanium (40 mm in diameter and 500 mm in length) was filled with 5.0 g (12 ml) of the catalyst used in Example 35. The catalyst was subjected to reducing treatment in a stream of hydrogen under 1 atmosphere at 350°C for 15 hours, and a gaseous mixture of CO and H_2 under pressure was passed through the catalyst layer and reacted. The products at the exit of the reactor were analyzed, and the results are shown in Table 15.

Table 15

	Example 41			
Catalyst	Rh-ThO_2-SiO_2			
Reaction conditions				
Pressure (kg/cm^2)	20	20	40	60
Temperature (°C)	230	250	260	270
CO/H_2 mole ratio	0.5	0.5	0.5	0.5
SV (h^{-1})	3840	7680	7680	11520
Feed (ml/min.)	800	1600	1600	2400
Composition of the products (mmoles/hr)				
CH_3OH	1.45	3.71	6.67	20.6
CH_3CHO	0.17	0.31	0.45	0.85
C_2H_2OH	1.50	3.65	6.83	18.0
CH_3COOH	0.44	1.05	1.71	3.09
n-C_3H_7OH	0.060	0.12	0.18	0.311
n-C_4H_9OH	trace	trace	trace	trace
C_1	1.15	3.04	4.08	9.62
C_2	0.028	0.072	0.10	0.175
C_3	0.054	0.079	0.10	0.166
C_4	trace	trace	reace	trace
CO_2	0.055	0.214	0.203	0.395
CO conversion (%)	1.1	1.4	2.3	3.9
CE (%)	80.1	79.5	84.0	85.7
STY	30	74	132	308

Example 42

Zirconium oxynitrate dihydrate (2.5 g) was dissolved in 100 ml of water, and 10 g of silica gel pellets (Davison #57; 8-10 mesh) were added to the solution. The impregnated silica gel pellets were heat-treated in the air at 500°C for a day and night in an electric furnace to obtain zirconium oxide-containing carrier. The product was dipped in a solution of 1.2 g of rhodium chloride trihydrate and 0.133 g of niobium chloride in 20 ml of ethanol. The ethanol was removed by a rotary evaporator, and 10 g of the $RhCl_3$-$NbCl_5$ supported product was packed into a flow-type reactor of Pyrex glass (18 mm in diameter and 500 mm in length). The temperature was gradually raised from room temperature while passing a helium-diluted hydrogen gas (1 atm., H_2:He=40:40, ml/min.) through the reactor, and finally the $RhCl_3$-$NbCl_5$ supported product was subjected to reducing treatment in hydrogen at 400°C overnight.

Using the resulting catalyst, a gaseous mixture consisting of CO, H_2 and He (CO:H_2:He=20:40:20, ml/min.) was reacted under a total pressure of 1 atm. The amounts of oxygen-containing hydrocarbon compounds and hydrocarbons formed at about 150 to 250°C were analyzed by the same method as in Example 35. The results are shown in Table 16.

Comparative Example 8

Rhodium chloride trihydrate (1.2 g) was deposited from its methanol solution on 10 g of silica gel (Davison #57), and reduced with hydrogen at 400°C by the same operation as in Example 42. Using 10 g of the resulting catalyst, the CO-H_2 reaction was carried out under atmospheric pressure in the same way as in Example 42. The results are also shown in Table 16.

Table 16

	Example 42				Comparative Example 8		
Catalyst	Rh-Nb/ZrO_2-SiO_2 (Rh 0.48 g, Nb 0.058) ZrO_2/SiO_2 = 11.4 wt%				Rh/SiO_2 (Rh 0.48 g)		
Reaction conditions							
SV (hr^{-1})	192	192	192	192	192	192	192
Temperature (°C)	200	190	200	185	264	278	245
CO/H_2 mole ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed (ml/min)	80	80	80	80	80	80	80
Amounts of the products (mmoles/hr)							
CH_3OH	0.026	0.024	0.031	0.009	-	-	0.01
CH_3CHO	0.094	0.062	0.077	0.042	0.027	0.008	0.029
C_2H_5OH	0.743	0.471	0.758	0.384	-	0.003	0.010
CH_3COOH	0.115	0.084	0.109	0.074	-	-	-
C_1	2.260	0.794	1.940	0.074	1.18	2.67	0.47
C_2	0.098	0.042	0.079	0.030	0.08	0.14	0.02
C_3	0.251	0.114	0.190	0.030	0.02	0.023	0.004
C_4	0.034	trace	0.022	trace	trace	trace	trace
CO_2	0.180	0.085	0.245	0.056	0.03	0.03	trace
CO conversion (mole %)	10.4	5.0	9.6	4.1	3.3	7.3	1.4
CE (%)	37.1	49.1	39.0	47.3	3.7	0.8	14.9
Ethanol selectivity (%)	77.0	75.0	79.0	76.1	- 0	27	22
STY	4.4	3.0	4.6	2.4	0.12	0.05	0.17

Example 43

Zirconium oxynitrate dihydrate (2.5 g) was deposited on 10 g of silica gel (Davison #57), and heat-decomposed at 500°C in an electric furnace to obtain a carrier containing zirconium. The carrier was dipped in a solution of 1.2 g of rhodium chloride trihydrate and 0.314 g of rhenium chloride in 100 ml of methanol. The solvent was removed by a rotary evaporator, and 10 g of the resulting product was packed into a flowing-type reactor, and subjected to reducing treatment in hydrogen at 400°C by the same operation as in Example 42. Using the resulting catalyst, the $CO-H_2$ reaction was carried out under atmospheric pressure in the same way as in Example 42. The results are shown in Table 17.

Example 44

Rhodium chloride trihydrate (1.2 g), zirconium oxynitrate dihydrate (2.5 g) and rhenium chloride (0.59 g) were successively dissolved in 100 ml of methanol. Ten grams of silica gel (Davison #57) was fully dipped in the resulting solution. The methanol was removed by a rotary evaporator. The resulting product was subjected to reducing treatment in hydrogen by the same operation as in Example 42. Using 10 g of the resulting catalyst, the $CO-H_2$ reaction was carried out under atmospheric pressure. The results are shown in Table 17.

Example 45

Ten grams of the same zirconium-containing carrier as used in Example 42 (prepared from 2.5 g of $ZrO(NO_3)_2 \cdot 2H_2O$ and 10 g of SiO_2 (Davison #57)) was fully dipped in a solution of 1.2 g of rhodium chloride trihydrate and 0.48 g of tantalum chloride in 20 ml of ethanol. The ethanol was removed by a rotary evaporator. The dried product was packed into a flowing-type reactor, and subjected to reducing treatment in hydrogen at 400°C by the same operation as in Example 42. Using 10 g of the resulting catalyst, the $CO-H_2$ reaction was carried out under atmospheric pressure. The results are shown in Table 17.

Example 46

The procedure of Example 45 was repeated except that the amount of tantalum chloride was changed to 0.78 g. The results are also shown in Table 17.

Table 17

Example	Catalyst	Reaction conditions SV (h^{-1})	Temperature (^{o}C)	CO/H_2 mole ratio	Feed (ml/min.)
43	$Rh-Re/ZrO_2-SiO_2$ (Rh 0.48 g, Re 0.16 g) ZrO_2/SiO_2 = 11.4 wt%	192	196	0.5	80
		192	211	0.5	80
44	$Rh-Re-ZrO_2/SiO_2$ (Rh 0.48 g, Re 0.30 g) ZrO_2/SiO_2 = 11.4 wt%	192	200	0.5	80
		192	190	0.5	80
45	$Rh-Ta/ZrO_2-SiO_2$ (Rh 0.48, Ta 0.24 g) ZrO_2/SiO_2 = 11.4 wt%	192	200	0.5	80
		192	200	0.5	80
		192	190	0.5	80
		192	210	0.5	80
46	$Rh-Ta/ZrO_2-SiO_2$ (Rh 0.43 g, Ta 0.40 g) ZrO_2/SiO_2 = 11.4 wt%	192	190	0.5	80
		192	180	0.5	80

- to be continued -

Table - 17 (continued)

Ex-ample	Amounts of the products (mmoles/hr)									CO conver-sion (%)	CE (%)	Ethanol selec-tivity (%)	STY
	CH_3OH	CH_3CHO	C_2H_5OH	CH_3COOH	C_1	C_2	C_3	C_4	CO_2				
43	0.046	trace	0.550	trace	0.567	0.036	0.039	trace	0.021	3.6	59.5	96.0	2.7
	0.089	trace	0.621	trace	1.500	0.098	0.102	0.026	0.051	6.7	38.2	93.3	3.1
44	0.097	0.084	1.051	trace	1.788	0.141	0.165	trace	0.037	9.8	45.0	92.8	5.5
	0.064	0.032	0.329	0.011	0.562	0.030	0.025	trace	0.029	3.2	52.5	82.0	1.9
45	0.059	0.079	0.612	0.075	1.339	0.045	0.145	trace	0.014	6.84	45.9	76.9	3.8
	0.039	0.140	0.602	0.094	1.164	0.034	0.116	trace	0.017	6.33	49.6	76.6	4.1
	0.041	0.052	0.405	0.056	0.430	0.013	0.049	trace	trace	3.14	63.8	75.8	2.6
	0.062	0.089	0.705	0.096	1.677	0.059	0.174	trace	0.027	8.10	44.0	76.5	4.4
46	0.036	0.073	0.722	0.113	1.744	0.043	0.171	0.011	0.021	8.5	43.5	78.0	4.5
	0.037	0.053	0.427	0.075	0.676	0.018	0.097	trace	0.020	4.3	52.8	74.5	2.8
	0.028	0.038	0.286	0.043	0.354	trace	0.041	trace	0.013	2.4	60.9	75.1	1.8

Example 47 and Comparative Example 9

Ten grams (25 ml) of the catalyst used in Example 44 was packed in a stainless steel pressure reactor lined with titanium (40 mm in diameter and 500 mm in length) and subjected to reducing treatment in a stream of hydrogen (1 atm.) at 350°C for 5 hours. Using the resulting catalyst, a gaseous mixture of CO and H_2 was passed through the catalyst layer and reacted under an elevated pressure. The products at the exit of the reactor were analyzed, and the results are shown in Table 18.

For comparison, a catalyst prepared by depositing rhodium chloride on silica was tested for activity in the reaction of a synthesis gas at low to medium pressures. The results are also shown in Table 18.

Table 18

Catalyst	Example 47 Rh-he-ZrO$_2$-SiO$_2$					Comparative Example 9 Rh/SiO$_2$	
Reaction conditions							
Gas pressure (kg/cm^2)	20	20	20	30	30	20	40
SV (hr^{-1})	1920	3840	5760	3840	5760	960	960
Temperature (^{o}C)	220	220	220	230	230	292	282
CO/H$_2$ mole ratio	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed (ml/min.)	800	1600	2400	1600	2400	800	800
Amount of the products (mmoles/hr)							
CH_3OH	4.32	16.4	20.2	39.5	45.4	0.04	0.04
CH_3CHO	trace	trace	trace	trace	trace	1.59	0.87
C_2H_5OH	2.76	12.62	13.8	25.3	26.1	0.91	0.24
CH_3COOH	0.27	1.00	1.23	2.57	1.88	trace	trace
C_3H_7OH	0.46	1.66	1.72	3.29	3.23	trace	trace
C_4H_9OH	trace	0.54	0.37	0.65	0.74	trace	trace
C_1	1.36	5.82	8.97	12.7	16.8	18.2	3.69
C_2	0.21	1.02	1.77	2.41	3.01	2.70	0.89
C_3	0.20	0.49	0.90	1.04	1.24	2.69	1.92
C_4	trace	trace	trace	trace	trace	0.12	1.04
CO_2	0.11	0.34	0.33	0.68	1.01		
CO conversion (%)	2.2	4.6	3.7	9.9	7.2	3.7	1.1
CE (%)	83.6	84.0	78.5	83.5	80.6	11.2	12.8
STY	30.5	131	149	283	339	12	5

Example 48

Twenty grams of silica gel (Davison #57) was fired at 300°C in vacuum. The fired silica gel was dipped in a solution of 5.3 g of titanium tetraisopropoxide in 100 ml of n-hexane. The n-hexane was evaporated off by a rotary evaporator. The dried product was heat-treated in an electric furnace at 200°C for 2 hours and then at 500°C for 2 days. Ten grams of the resulting carrier was dipped in a solution of 1.2 g of rhodium chloride trihydrate and 0.25 g of rhenium chloride in 100 ml of methanol. The methanol was removed under high vacuum.

Ten grams of the product containing rhodium chloride and rhenium chloride deposited thereon was packed into the same reactor as in Example 42, and subjected to reducing treatment in a stream of hydrogen first at 100°C for 1 hour and then at 300°C overnight. Using the resulting catalyst, the $CO-H_2$ reaction was carried out in the same way as in Example 42. The results are shown in Table 19.

Table 19

	Example 48	
Catalyst	$Rh-Re/TiO_2-SiO_2$ (Rh 0.48 g, Re 0.128 g) TiO_2/SiO_2 = 15.7 wt%	
Reaction conditions		
SV (hr^{-1})	193	978
Temperature (^oC)	182	180
CO/H_2 mole ratio	0.5	0.5
Feed (ml/min.)	79	400
Amounts of the products (mmoles/hr)		
CH_3OH	0.145	0.099
CH_3CHO	0.055	0.066
C_2H_5OH	1.197	1.392
CH_3COOH	0.053	0.015
C_3H_7OH	0.013	0.024
C_1	1.301	1.406
C_2	0.103	0.104
C_3	0.201	0.225
C_4	0.111	0.130
CO_2	0.056	0.104
CO conversion (mole %)	10.1	2.3
CE (%)	51.7	51.7
Ethanol selectivity (%)	85.7	89.3
STY	6.6	7.3

Example 49

Rhodium chloride trihydrate (1.2 g) and 0.2 g of rhenium chloride were dissolved in 100 ml of methanol. A zirconium oxide-silica carrier obtained from 2.3 g of zirconium oxynitrate dihydrate and 10 g of silica gel (Davison #57) by heat decomposition at 500°C in the air was dipped fully in the resulting solution. The methanol was removed by a rotary evaporator, and 10 g of the resulting product was packed into a flowing-type reactor, and subjected to a reducing treatment using a gaseous mixture of 40 ml/min. of hydrogen and 40 ml/min. of helium at 400°C for 15 hours.

A gaseous mixture consisting of CO, CO_2 and H_2 was passed through the catalyst layer, and reacted. The amounts of the products yielded per hour were examined, and the results are shown in Table 20.

Table 20

	Example 49	
Catalyst	$Rh-Re/ZrO_2-SiO_2$ (Rh 0.48 g, Re 0.10 g) ZrO_2/SiO_2 = 11.4 wt%	
Temperature (°C)	190	190
Feed composition (ml/min.)		
CO	20	15
H_2	40	40
He	20	20
CO_2	5	5
Amounts of the products (mmoles/hr)		
CH_3OH	0.030	0.028
CH_3CHO	0.032	0.034
C_2H_5OH	0.397	0.388
CH_3COOH	-	0.005
C_1	0.465	0.281
C_2	0.040	0.041
C_3	0.042	0.032
C_4	0.012	0.012
CE (%)	54.3	62.4

CLAIMS

1. A process for producing compounds containing oxygen, hydrogen and carbon having 1 or 2 carbon atoms by reacting a gaseous mixture of a carbon oxide and hydrogen in the presence of a rhodium-containing hydrogenation catalyst, characterised in that the hydrogenation catalyst is a catalyst composition comprising

(A) substantially metallic rhodium and

(B) an oxide of a metal of Group IIa, IIIa, IVa or Va of the Periodic Table of short form.

2. A process according to claim 1 characterised in that said metallic rhodium has been formed from a simple salt of rhodium.

3. A process according to claim 1 or 2 charaterised in that the amount of metallic rhodium is 0.0001 to 50% by weight based on the weight of the catalyst composition.

4. A process according to claim 1, 2 or 3 characterised in that the oxide (B) is an oxide of a metal selected from magnesium, calcium, lanthanum, neodymium, cerium, yttrium, thorium, titanium, zirconium, niobium and tantalum.

5. A process according to any one of the preceding claims characterised in that catalyst composition also includes silica.

6. A process according to claim 5 characterised in that the weight ratio of the metal oxide (B) to silica is from 100:1 to 1:100.

7. A process according to claim 5 or 6 characterised in that the amount of silica is 0.001 to 99.9% by weight based on the weight of said catalyst composition.

8. A process according to any one of the preceding claims characterised in that the reaction is carried out at a temperature of 50 to 450°C and a pressure of 0.5 to 350 atmospheres (gauge) at a space velocity of 10 to 10^6 liters/liter hr^{-1}.

9. A process according to any one of the preceding claims characterised in that the carbon oxide is carbon monoxide.

10. A process according to any one of the preceding claims characterised in that the mole ratio of carbon oxide to hydrogen in the gaseous mixture is from 20:1 to 1:20.

11. A process according to any one of the preceding claims characterised in that the catalyst composition also comprises (C) an element selected from niobium, tantalum, chromium, manganese and rhenium, and the metal oxide (B) is an oxide of a metal of Group IIIa, IVa or Va.

12. A process according to claim 11 characterised in that the weight ratio of metallic rhodium to said metal element (C) is from 10:1 to 1:10.

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EUROPEAN SEARCH REPORT

Application number
EP 80 30 2264

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 2 317 260 (U.C.) * Page 23, line 12 - page 24, line 23; claims * --	1-12
	US - A - 4 096 164 (P.C. ELLGEN et al.) * Whole patent * --	1-12
	US - A - 3 929 969 (E.S. BROWN) * Whole patent; column 12, lines 1-19 * --	1-12
	US - A - 3 974 259 (E.S. BROWN) * Whole patent; column 12, lines 31-49 * --	1-12
	US - A - 3 989 799 (E.S. BROWN) * Whole patent; column 11, line 67 - column 12, line 17 * --	1-12
	US - A - 3 878 290 (W.E. WALKER et al.) * Whole patent * --	1-12
	US - A - 3 878 214 (W.E. WALKER et al.) * Whole patent * -- ./.	1-12

CLASSIFICATION OF THE APPLICATION (Int Cl.3)

C 07 C 27/06
31/08
47/06
31/04
29/15
45/49

TECHNICAL FIELDS SEARCHED (Int. Cl.3)

C 07 C 29/15
45/49

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
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corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	06-10-1980	DELHOMME

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EUROPEAN SEARCH REPORT

Application number
EP 80 30 2264

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	PATENT ABSTRACTS OF JAPAN, vol. 3, no. 68, 13th June 1973, page 48C48 & JP - A - 54 41291 --	1-12
	FR - A - 2 234 256 (U.C.) * Page 5, lines 9-30; page 20, line 4 - page 21, line 14; claims 1-16 * --	1-12
P,X	US - A - 4 162 262 (P.C. ELLGEN) * Whole patent * --	1-12
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CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

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