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(54) Title: NICKEL-RHODIUM BASED CATALYSTS AND PROCESS FOR PREPARING SYNTHESIS GAS

(57) Abstract: A process for preparing a product gas mixture comprising CO and H<sub>2</sub> from a light hydrocarbon and O<sub>2</sub> mixture is disclosed. The process includes contacting a reactant gas mixture comprising a C<sub>1</sub>-C<sub>5</sub> hydrocarbon and a source of molecular oxygen with a catalytically effective amount of a supported catalyst comprising nickel and rhodium. The catalyst and reactant gas mixture is maintained at catalytic partial oxidation promoting conditions of temperature and pressure during the contacting period, which is preferably 10 milliseconds or less. Certain preferred catalysts comprise an alloy of about 1-50 weight percent nickel and about 0.01-10 weight percent rhodium and optionally lanthanide elements, zirconium, cobalt, manganese and magnesium on a porous refractory support structure.



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## NICKEL-RHODIUM BASED CATALYSTS AND PROCESS FOR PREPARING SYNTHESIS GAS

### CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims the benefit of U.S. Provisional Patent Application No. 60/160,100 filed October 18, 1999, the disclosure of which is incorporated herein by reference.

### BACKGROUND OF THE INVENTION

#### Field of the Invention

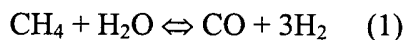
10 The present invention relates to processes for producing synthesis gas from light hydrocarbons (e.g., natural gas) and oxygen. More particularly, the invention relates to supported nickel-rhodium based catalysts, their methods of making, and to processes employing such catalysts for net partial oxidation of light hydrocarbons (e.g., natural gas) to products comprising CO and H<sub>2</sub>.

#### 15 Description of Related Art

Large quantities of methane, the main component of natural gas, are available in many areas of the world, and natural gas is predicted to outlast oil reserves by a significant margin. However, most natural gas is situated in areas that are geographically remote from population and industrial centers. The costs of compression, transportation, and storage make its use  
20 economically unattractive.

To improve the economics of natural gas use, much research has focused on methane as a starting material for the production of higher hydrocarbons and hydrocarbon liquids. The conversion of methane to hydrocarbons is typically carried out in two steps. In the first step, methane is reformed with water to produce carbon monoxide and hydrogen (i.e., synthesis gas  
25 or syngas). In a second step, the syngas is converted to hydrocarbons, for example, using the Fischer-Tropsch process to provide fuels that boil in the middle distillate range, such as kerosene and diesel fuel, and hydrocarbon waxes.

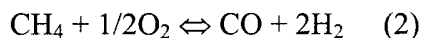
Current industrial use of methane as a chemical feedstock proceeds by the initial conversion of methane to carbon monoxide and hydrogen by either steam reforming, which is  
30 the most widespread process, or by dry reforming. Steam reforming currently is the major process used commercially for the conversion of methane to synthesis gas, proceeding according to Equation 1.



Although steam reforming has been practiced for over five decades, efforts to improve the energy efficiency and reduce the capital investment required for this technology continue.

The catalytic partial oxidation of hydrocarbons, e.g., natural gas or methane to syngas is also a process known in the art. While currently limited as an industrial process, partial oxidation has recently attracted much attention due to significant inherent advantages, such as the fact that significant heat is released during the process, in contrast to steam reforming processes.

In catalytic partial oxidation, natural gas is mixed with air, oxygen-enriched air, or oxygen, and introduced to a catalyst at elevated temperature and pressure. The partial oxidation of methane yields a syngas mixture with a H<sub>2</sub>:CO ratio of 2:1, as shown in Equation 2.



This ratio is more useful than the H<sub>2</sub>:CO ratio from steam reforming for the downstream conversion of the syngas to chemicals such as methanol and to fuels. The partial oxidation is also exothermic, while the steam reforming reaction is strongly endothermic. Furthermore, oxidation reactions are typically much faster than reforming reactions. This allows the use of much smaller reactors for catalytic partial oxidation processes. The syngas in turn may be converted to hydrocarbon products, for example, fuels boiling in the middle distillate range, such as kerosene and diesel fuel, and hydrocarbon waxes by processes such as the Fischer-Tropsch Synthesis.

The selectivities of catalytic partial oxidation to the desired products, carbon monoxide and hydrogen, are controlled by several factors, but one of the most important of these factors is the choice of catalyst composition. Difficulties have arisen in the prior art in making such a choice economical. Typically, catalyst compositions have included precious metals and/or rare earths. The large volumes of expensive catalysts needed by prior art catalytic partial oxidation processes have placed these processes generally outside the limits of economic justification.

For successful operation at commercial scale, the catalytic partial oxidation process must be able to achieve a high conversion of the methane feedstock at high gas hourly space velocities, and the selectivity of the process to the desired products of carbon monoxide and hydrogen must be high. Such high conversion and selectivity must be achieved without detrimental effects to the catalyst, such as the formation of carbon deposits ("coke") on the catalyst, which severely reduces catalyst performance. Accordingly, substantial effort has

been devoted in the art to the development of catalysts allowing commercial performance without coke formation.

A number of process regimes have been proposed in the art for the production of syngas via catalyzed partial oxidation reactions. For example, the process described in U.S. Pat. No. 4,877,550 employs a syngas generation process using a fluidized reaction zone. Such a process however, requires downstream separation equipment to recover entrained supported-nickel catalyst particles.

To overcome the relatively high pressure drop associated with gas flow through a fixed bed of catalyst particles, which can prevent operation at the high gas space velocities required, various structures for supporting the active catalyst in the reaction zone have been proposed. U.S. Pat. No. 5,510,056 discloses a monolithic support such as a ceramic foam or fixed catalyst bed having a specified tortuosity and number of interstitial pores that is said to allow operation at high gas space velocity. Catalysts used in that process include ruthenium, rhodium, palladium, osmium, iridium, and platinum. Data are presented for a ceramic foam supported rhodium catalyst at a rhodium loading of from 0.5-5.0 wt %.

U.S. Pat. No. 5,648,582 discloses a process for the catalytic partial oxidation of methane at space velocities of  $800,000 \text{ hr}^{-1}$  to  $12,000,000 \text{ hr}^{-1}$  on certain supported Rh, Ni or Pt catalysts. The exemplified catalysts are rhodium and platinum, at a loading of about 10 wt %, on alumina foams. The small catalyst bed used in this process is said to eliminate hot spots which are typical of relatively thick catalyst beds.

Catalysts containing Group VIII metals such as nickel or rhodium on a variety of supports are known in the art. For example, V. R. Choudhary et al. ("Oxidative Conversion of Methane to Syngas over Nickel Supported on Low Surface Area Catalyst Porous Carriers Precoated with Alkaline and Rare Earth Oxides," *J. Catalysis* 172:281-293 (1997)) disclose the partial oxidation of methane to syngas at contact times of 4.8 ms (at STP) over supported nickel catalysts at 700 and 800°C. The catalysts were prepared by depositing NiO-MgO on different commercial low surface area porous catalyst carriers consisting of refractory compounds such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , SiC,  $\text{ZrO}_2$  and  $\text{HfO}_2$ . The catalysts were also prepared by depositing NiO on the catalyst carriers with different alkaline and rare earth oxides such as MgO, CaO, SrO, BaO,  $\text{Sm}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$ .

U.S. Pat. No. 4,690,777 also discloses catalysts comprising Group VIII metals, such as Ni, on porous supports, for use in reforming hydrocarbons to produce CO and  $\text{H}_2$ .

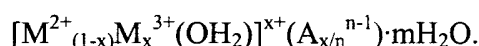
U.S. Pat. No. 5,149,464 discloses a method for selectively converting methane to syngas at 650°C to 950°C by contacting the methane/oxygen mixture with a solid catalyst comprising a supported d-Block transition metal, transition metal oxide, or a compound of the formula  $M_xM'_yO_z$  wherein  $M'$  is a d-Block transition metal and  $M$  is Mg, B, Al, Ga, Si, Ti, 5  
Xr, Hf or a lanthanide.

U.S. Pat. No. 5,500,149 discloses various transition metals that can act as catalysts in the reaction  $CO_2 + CH_4 \rightarrow 2CO + 2H_2$ , and demonstrates how reaction conditions can affect the product yield.

The partial oxidation of methane to synthesis gas using various transition metal catalysts under a range of conditions has been described by Vernon, D.F. et al. (*Catalysis Letters* 6:181-186 (1990)). European Pat. App. Pub. No. 640561 discloses a catalyst for the catalytic partial oxidation of hydrocarbons comprising a Group VIII metal on a refractory oxide having at least two cations.

U.S. Pat. No. 5,447,705 discloses a catalyst having a perovskite crystalline structure and the general composition:  $Ln_xA_{1-y}B_yO_3$ , wherein  $Ln$  is a lanthanide and  $A$  and  $B$  are 15  
different metals chosen from Group IVb, Vb, VIb, VIIb or VIII of the Periodic Table of the Elements.

U.S. Pat. No. 5,653,774 discloses a nickel-containing catalyst for preparing synthesis gas which are prepared by heating hydrotalcite-like compositions having the general formula:



A previous attempt at synthesis gas production by catalytic partial oxidation to overcome some of the disadvantages and costs typical of steam reforming is described in European Patent No. EPO 0 303 438, entitled "Production of Methanol from Hydrocarbonaceous Feedstock."

One disadvantage of many of the existing catalytic hydrocarbon conversion methods is the need to include steam in the feed mixture to suppress coke formation on the catalyst. Another drawback of some of the existing processes is that the catalysts that are employed often result in the production of significant quantities of carbon dioxide, steam, and  $C_2+$  hydrocarbons. Also, large volumes of expensive catalyst are typically required in order to 25  
achieve satisfactory conversion of the feed gas, and to achieve the necessary level of selectivity for CO and  $H_2$  products. None of the existing processes or catalysts are capable of providing high conversion of reactant gas and high selectivity of CO and  $H_2$  reaction products. Accordingly, there is a continuing need for a process and catalyst for the catalytic partial

oxidation of hydrocarbons, particularly methane, or methane containing feeds, in which the catalyst retains a higher level of activity and selectivity to carbon monoxide and hydrogen under conditions of high gas space velocity, elevated pressure and high temperature.

### SUMMARY OF THE INVENTION

5           The present invention provides catalysts and processes for preparing synthesis gas from any gaseous hydrocarbon having a low boiling point (e.g. C<sub>1</sub>-C<sub>5</sub> hydrocarbons, particularly methane, or methane containing feeds) and a source of molecular oxygen. One advantage of the new catalysts is that they retain a high level of activity and selectivity to carbon monoxide and hydrogen under conditions of high gas space velocity, elevated pressure  
10           and high temperature.

          The new processes of the invention are particularly useful for converting gas from naturally occurring reserves of methane which contain carbon dioxide. Another advantage of the new catalysts and processes is that they are economically feasible for use in commercial-scale conditions. In a short contact time reactor, the new Ni-Rh based catalysts are highly  
15           active for catalyzing the oxidation of methane to syngas by an overall or net partial oxidation process. "Net partial oxidation" means that the partial oxidation reaction predominates over reforming reactions, and the ratio of the H<sub>2</sub>:CO products is about 2. The short contact time reactor permits the reactant gas mixture to contact or reside on the catalyst for no longer than about 10 milliseconds, operating at high space velocities.

20           In accordance with certain embodiments of the present invention a supported catalyst is provided for catalyzing the net partial oxidation of a hydrocarbon. The supported catalyst contains about 1-50 weight percent nickel and about 0.01-10 weight percent rhodium, and a support structure. Preferably, the support structure comprises a spinel, a perovskite, magnesium oxide, a pyrochlore, a brownmillerite, zirconium phosphate, magnesium  
25           stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet, alumina, cordierite, ZrO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub> or TiO<sub>2</sub>. The rhodium and nickel are disposed on or within the support structure. In some of the more preferred embodiments, the catalyst support structure is a spinel, a perovskite, a pyrochlore or a brownmillerite, and the nickel-rhodium alloy is incorporated  
30           into the support structure. In some embodiments the catalyst comprises a solid solution of rhodium-nickel-magnesium-oxide.

          In certain embodiments of the catalysts the support structure comprises a refractory oxide, which may be in the form of a foam structure. Preferably such a foam structure

comprises about 12-60 pores per centimeter of structure. Alternatively, the support structure may be in the form of a honeycomb monolith structure.

In some embodiments, the catalyst comprises a mixture of rhodium and nickel on a support structure comprising  $\text{Al}_2\text{O}_3$ . Some embodiments comprise an alloy of 1% rhodium, 3% manganese and 13% nickel on a  $\text{MgAl}_2\text{O}_4$  support structure. In some embodiments the catalyst comprises 1% rhodium and  $\text{LaZr}_{0.5}\text{Ni}_{0.5}\text{O}_3$  (expressed as stoichiometric amounts). Another catalyst embodiment comprises  $\text{Rh}_{0.02}\text{Ni}_{0.03}\text{Mg}_{0.95}\text{O}$ , and yet another comprises rhodium, nickel and cobalt on a support structure comprising  $\text{ZrO}_2$ . Certain catalysts of the invention comprise 1% rhodium, 10.9% nickel and 8.6% magnesium on a support structure comprising 99%  $\text{Al}_2\text{O}_3$ .

Also provided by the present invention are processes for the net partial oxidization of a 1-5 carbon containing hydrocarbon to form a product gas mixture comprising CO and  $\text{H}_2$ . In some embodiments the process comprises contacting a reactant gas mixture comprising the hydrocarbon and a source of oxygen with a catalytically effective amount of a Ni-Rh alloy-containing catalyst having a composition as described above. The process also includes maintaining the catalyst and the reactant gas mixture at conversion promoting conditions of temperature, gas flow rate and feed composition during contact with the reactant gas mixture. Preferably the process includes maintaining the reactant gas mixture and the catalyst at a temperature of about 600-1,200°C during contact. In some embodiments the temperature is maintained at about 700-1,100°C.

In some embodiments of the process the reactant gas mixture and the catalyst are maintained at a pressure of about 100-12,500 kPa during the contacting, and in some of the more preferred embodiments the pressure is maintained at about 130-10,000 kPa.

Certain embodiments of the processes for converting hydrocarbons to CO and  $\text{H}_2$  comprise mixing a methane-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1. In some of these embodiments, the mixing step is such that it yields a reactant gas mixture feed having a carbon:oxygen ratio of about 1.3:1 to about 2.2:1, or about 1.5:1 to about 2.2:1. In some of the most preferred embodiments the mixing step provides a reactant gas mixture feed having a carbon:oxygen ratio of about 2:1.

In some embodiments of the processes the said oxygen-containing gas that is mixed with the hydrocarbon comprises steam or  $\text{CO}_2$ , or a mixture of both. In some embodiments of the processes the  $\text{C}_1\text{-C}_5$  hydrocarbon comprises at least about 50 % methane by volume, and

in some of the preferred embodiments the C<sub>1</sub>-C<sub>5</sub> hydrocarbon comprises at least about 80 % methane by volume.

Certain embodiments of the processes for preparing synthesis gas comprise preheating the reactant gas mixture. Some embodiments of the processes comprise passing the reactant gas mixture over the catalyst at a space velocity of about 20,000 to about 100,000,000 normal  
5 liters of gas per kilogram of catalyst per hour (NL/kg/h). In certain of these embodiments, the gas mixture is passed over the catalyst at a space velocity of about 50,000 to about 50,000,000 NL/kg/h. Preferably the residence time of the reactant gas mixture on the catalyst is no more than about 10 milliseconds duration.

10 In some embodiments of the processes of the present invention the catalyst is retained in a fixed bed reaction zone. These and other embodiments, features and advantages of the present invention will become apparent with reference to the following description.

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15 Preferred Ni-Rh based catalysts for catalytically converting C<sub>1</sub>-C<sub>5</sub> hydrocarbons to CO and H<sub>2</sub> comprise an alloy of about 1 wt% to about 50 wt% nickel and 0.01 to 10 wt% rhodium on supports of spinels, perovskites, magnesium oxide, pyrochlores, brownmillerites, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet,  
20 alumina, cordierite, ZrO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub> or TiO<sub>2</sub>. The Rh and/or Ni may be incorporated into the structure of the spinel, perovskite, pyrochlore or brownmillerite. Alternatively, a solid solution of Rh-Ni-Mg-oxide may be used. Preferably the catalyst is a Ni-Rh alloy. A Rh-Ni based catalyst is prepared as described in the following examples and utilizing techniques known to those skilled in the art, such as impregnation, wash coating, adsorption,  
25 ion exchange, precipitation, co-precipitation, deposition precipitation, sol-gel method, slurry dip-coating, microwave heating, and the like, or any of the other methods known in the art. Preferred techniques are impregnation, sol-gel methods and co-precipitation. For example, a Rh-Ni based catalyst is prepared by impregnation of a ceramic foam of a refractory oxide with rhodium and nickel.

30 Alternatively, the catalyst components, with or without a ceramic support composition, may be extruded to prepare a three-dimensional form or structure such as a honeycomb, foam, or other suitable tortuous-path structure. Additionally the catalyst components may be added to the powdered ceramic composition and then extruded to prepare



the foam or honeycomb. Suitable foams for use in the preparation of the catalyst include those having from 30 to 150 pores per inch (12 to 60 pores per centimeter). Alternative forms for the catalyst include refractory oxide honeycomb monolith structures, or other configurations having longitudinal channels or passageways permitting high space velocities with a minimal pressure drop. Such configurations are known in the art and described, for example, in *Structured Catalysts and Reactors*, A. Cybulski and J.A. Moulijn (Eds.), Marcel Dekker, Inc., 1998, p. 599-615 (Ch. 21, X. Xu and J.A. Moulijn, "Transformation of a Structured Carrier into Structured Catalyst")

Any suitable reaction regime may be applied in order to contact the reactants with the catalyst. One suitable regime is a fixed bed reaction regime, in which the catalyst is retained within a reaction zone in a fixed arrangement. Particles of catalyst may be employed in the fixed bed regime, retained using fixed bed reaction techniques well known in the art. Alternatively, the catalyst may be in the form of a foam, or porous monolith.

### ***Process of Producing Syngas***

A feed stream comprising a hydrocarbon feedstock and an oxygen-containing gas is contacted with one of the above-described Rh-Ni alloy catalysts in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising carbon monoxide and hydrogen. Preferably a millisecond contact time reactor is employed. The hydrocarbon feedstock may be any gaseous hydrocarbon having a low boiling point, such as methane, natural gas, associated gas, or other sources of light hydrocarbons having from 1 to 5 carbon atoms. The hydrocarbon feedstock may be a gas arising from naturally occurring reserves of methane which contain carbon dioxide. Preferably, the feed comprises at least 50% by volume methane, more preferably at least 75% by volume, and most preferably at least 80% by volume methane.

The hydrocarbon feedstock is in the gaseous phase when contacting the catalyst. The hydrocarbon feedstock is contacted with the catalyst as a mixture with an oxygen-containing gas, preferably pure oxygen. The oxygen-containing gas may also comprise steam and/or CO<sub>2</sub> in addition to oxygen. Alternatively, the hydrocarbon feedstock is contacted with the catalyst as a mixture with a gas comprising steam and/or CO<sub>2</sub>.

Preferably, the methane-containing feed and the oxygen-containing gas are mixed in such amounts to give a carbon (i.e., carbon in methane) to oxygen (i.e., oxygen) ratio from about 1.25:1 to about 3.3:1, more preferably, from about 1.3:1 to about 2.2:1, and most preferably from about 1.5:1 to about 2.2:1, especially the stoichiometric ratio of 2:1.

The process is operated at atmospheric or superatmospheric pressures, the latter being preferred. The pressures may be from about 100 kPa to about 12,500 kPa, preferably from about 130 kPa to about 10,000 kPa.

5 The process is preferably operated at temperatures of from about 60 °C to about 1200°C, preferably from about 700°C to about 1100°C. The hydrocarbon feedstock and the oxygen-containing gas are preferably pre-heated before contact with the catalyst.

10 The hydrocarbon feedstock and the oxygen-containing gas are passed over the catalyst at any of a variety of space velocities. Space velocities for the process, stated as normal liters of gas per kilogram of catalyst per hour, are from about 20,000 to about 100,000,000 NL/kg/h, preferably from about 50,000 to about 50,000,000 NL/kg/h. Preferably the catalyst is employed in a millisecond contact time reactor for syngas production. The product gas mixture emerging from the reactor is collected and analyzed for CH<sub>4</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, CO<sub>2</sub>, etc.

### EXAMPLES

#### ***Catalyst Preparation***

15 Exemplary and comparative catalysts were prepared with and without the inclusion of rhodium, as described Examples 1-12, below. In these examples, calcining was conducted according to the following program: heat at a rate of 10°C/min. up to within about 50° of the target temperature, hold about 30 min., then heat at a rate of 1 °C/min up to the desired final temperature. Catalyst activities were tested in partial oxidation reactions at defined high gas  
20 hourly space velocities, temperature and feed composition. The level of CH<sub>4</sub> conversion and selectivities to CO and H<sub>2</sub> products are reported below.

#### **Example 1: 3% Mn, 13% Ni/MgAl<sub>2</sub>O<sub>4</sub>**

25 The 3% Mn, 13% Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst was prepared by dissolving Ni (NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (19.325 g) and Mn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (4.702 g) in distilled water (50 ml) and wet impregnating calcined (600°C for 3 hours) MgAl<sub>2</sub>O<sub>4</sub> (25.2 g). The slurry was mixed with a spatula, dried at 110°C and calcined at 800°C for 2 hours. A portion of the calcined material (15 g) was reduced in flowing hydrogen (about 100 cc/minute) for 4 hours at 800°C

30

#### **Example 2: 1% Rh added to 3% Mn, 13% Ni/MgAl<sub>2</sub>O<sub>4</sub>**

Rh (III) chloride (0.264 g) was dissolved in 250 ml of acetone and 5 ml of water. The catalyst of 3% Mn, 13% Ni on MgAl<sub>2</sub>O<sub>4</sub> (10 g) was added to the solution and acetone was

evaporated off. The solid was calcined at 600°C for 1 hr and then reduced at 600°C for 4 hours with 10% H<sub>2</sub> in N<sub>2</sub> at a flow of 100 ml/min. High Resolution Transmission Electron Microscopy (HRTEM) and X-ray Adsorption Spectroscopy (XAS) analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

5

**Example 3: LaZr<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>3</sub>**

To a round bottom flask was added 61.61 g of ZrO<sub>2</sub>, 100 ml of 1M La(NO<sub>3</sub>)<sub>3</sub> and 50 ml of 1M Ni(NO<sub>3</sub>)<sub>2</sub>. The water was removed from the mixture on a rotoevaporator and dried in a vacuum oven. Calcination was carried out at 900°C for 100 hours with daily grinding and mixing.

10

**Example 4: 1% Rh on LaZr<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>3</sub>**

Rh (III) chloride (0.0176 g) was dissolved in 50 ml of acetone and 1 ml of water. The catalyst of LaZr<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>3</sub> (0.6811 g) was added to the solution and acetone was evaporated off. The solid was calcined at 600°C for 1 hr and then reduced at 600°C for 4 hours with 10% H<sub>2</sub> in N<sub>2</sub> at a flow of 100 ml/min. HRTEM and XAS analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

15

**Example 5: Ni<sub>0.03</sub>Mg<sub>0.97</sub>O**

The nickel magnesia solid solution was prepared by the co-precipitation method. From a mixed aqueous solution (1 L) of 4.50 g of nickel acetate tetrahydrate and 150.38 g of magnesium nitrate hexahydrate, their mixed carbonate was deposited by adding (1L) 3 M potassium carbonate aqueous solution at 60°C. After being filtered and washed with hot water, the precipitate was dried overnight at 120°C for 12 hours, and then calcined in air at 950°C for 10 h to yield 25 g of catalyst. The catalyst was reduced by hydrogen at 850°C for 0.5 h.

20

25

**Example 6: Rh<sub>0.02</sub>Ni<sub>0.03</sub>Mg<sub>0.95</sub>O**

An acetone solution of 1.93 g of rhodium acetylacetonate complex was impregnated onto 10 g of the calcined Ni<sub>0.03</sub>Mg<sub>0.97</sub>O. The solvent was evaporated off at room temperature and the solid material was calcined in air at 950°C for 10 hours and then reduced by hydrogen at 850°C for 0.5 h. HRTEM and XAS analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

30

**Example 7: Co, Ni /ZrO<sub>2</sub>**

A mixture containing 2.24 g of Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and 2.22 g of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O was prepared. To this mixture was added sufficient water to give a final volume of 15 ml. The resulting solution was added to 30 g of ZrO<sub>2</sub> (1/8" pellets, dried at 110°C). The "wet" pellets were air dried with stirring every 4 hours to ensure uniform drying. The air-dried pellets were calcined in air at 600°C for 3 hours.

**Example 8: Co, Ni, Rh /ZrO<sub>2</sub>**

A mixture containing 2.22 g of Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 2.23 g of Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and 12.63 g of a 10% solution of Rh(NO<sub>3</sub>)<sub>3</sub> was prepared. To this mixture was added sufficient water to give a final volume of 15 ml. The resulting solution was added to 30 g of ZrO<sub>2</sub> (1/8" pellets, dried at 110°C). The "wet" pellets were air dried with stirring every 4 hours to ensure uniform drying. The air-dried pellets were calcined in air at 600°C for 3 hours. HRTEM and XAS analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

**Example 9: NiAl<sub>2</sub>O<sub>4</sub>**

Al(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O (3.75g) and 1.45g Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O (1.45g) were dissolved in 10 ml distilled H<sub>2</sub>O with 0.1g of polyvinyl alcohol added for improved viscosity. To 1g of alpha alumina spheres (diameter 2 mm) was added 2 mL of this solution. The solvent was removed with a rotoevaporator at high temperature and the resulting material was calcined at 800°C for 2 hrs. HRTEM analysis confirmed formation of NiAl<sub>2</sub>O<sub>4</sub>.

**Example 10: 1% Rh/NiAl<sub>2</sub>O<sub>4</sub>**

NiAl<sub>2</sub>O<sub>4</sub> (0.8025g) was impregnated with a solution of 0.0208g of RhCl<sub>3</sub> 3H<sub>2</sub>O dissolved in 0.15g of H<sub>2</sub>O and 2.0g of acetone. The solvent was evaporated off at room temperature and the resulting material was dried in a vacuum oven over night at 110°C and then calcined at 600°C for 1 hour. Subsequent reduction was carried out at 600°C for 4 hours with 90 mL/min N<sub>2</sub> and 10 mL/min H<sub>2</sub>. HRTEM and XAS analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

**Test Procedure for Examples 1-10**

The catalysts were evaluated in a laboratory scale short contact time reactor, i.e., a 25 cm long x 4 mm i.d. quartz tube reactor equipped with a co-axial quartz thermocouple well. The void space within the reactor was packed with quartz chips. The catalyst bed was positioned with quartz wool at about the mid-length of the reactor. The catalyst bed was heated with a 4 inch (10.2 cm) 600 watt band furnace at 90% electrical output. All runs were done at a CH<sub>4</sub>:O<sub>2</sub> molar ratio of 2:1 and at a pressure of 5 psig (136 kPa). The reactor effluent was analyzed using a gas chromatograph equipped with a thermal conductivity detector. The C, H and O mass balance were all between 98% and 102%. The runs were conducted over two operating days with 6 hours of run time each day. The comparative results of these runs are shown in **Table 1**, wherein gas hourly space velocity is indicated by "GHSV." As shown in **Table 1**, no evidence of catalyst deactivation occurred after 12 hours. The comparative sets of examples, with and without Rh, show that the inclusion of Rh into the respective catalyst compositions resulted in higher CH<sub>4</sub> conversion and selectivities to CO and H<sub>2</sub> and lower catalyst bed temperatures.

**Table 1**

Ex.	Temp °C	GHSV x 10 <sup>5</sup>	% CH <sub>4</sub> / % O <sub>2</sub> Conv.	% CO / % H <sub>2</sub> Sel.	H <sub>2</sub> : CO
1	850	3.045	92 / 100	99 / 97	1.96
1	850	6.09	86 / 100	94 / 90	1.91
2	700	3.045	99 / 100	100 / 100	2.0
2	700	6.09	91 / 100	99 / 100	2.02
3	875	1.523	57 / 99	87 / 77	1.77
4	720	3.48	88 / 100	98 / 99	2.02
4	720	5.916	83 / 100	96 / 94	1.96
5	830	3.045	67 / 95	95 / 78	1.64
6	810	3.045	91 / 100	98 / 97	1.98
7	820	1.826	81 / 100	93 / 91	1.96
8	795	1.826	90/100	97/97	2.00
9	725	2.436	76/96	94/83	1.77
10	650	2.436	82/100	100/92	1.84

**Example 11: 12.7% Ni, 8.2% Mg on 99% Al<sub>2</sub>O<sub>3</sub> (12 mm OD x 10 mm ceramic foam of 80 ppi)**

The Al<sub>2</sub>O<sub>3</sub> monolith (1.1688g) was first impregnated with a solution of 1.3839 g of Mg(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O in 1 mL of H<sub>2</sub>O followed by evaporating off the solvent at room temperature, drying in a vacuum oven at 110°C for overnight, then calcining at 900°C for 4 hrs. The monolith was subsequently impregnated with one half the volume of a solution of 0.9990g of Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O dissolved in 2 mL of water. The solvent was evaporated off at room temperature, dried in a vacuum oven at 110°C overnight, and calcined at 600°C for 1 hr. The impregnation procedure was repeated with the remaining Ni nitrate solution and again the impregnated monolith was dried in a vacuum oven at 110°C overnight and calcined at 600°C for 1 hr.

**Example 12: 1% Rh, 10.9% Ni, 8.6% Mg on 99% Al<sub>2</sub>O<sub>3</sub> (12 mm OD x 10 mm ceramic foam of 80 ppi)**

The Al<sub>2</sub>O<sub>3</sub> monolith (1.1356g) was first impregnated with a solution of 1.3997g of Mg(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O in 1 mL of H<sub>2</sub>O followed by evaporating off the solvent at room temperature, drying in a vacuum oven at 110°C overnight, then calcining at 900°C for 4 hrs. The monolith was subsequently impregnated with one half the volume of a solution of 0.8308g of Ni(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O dissolved in 2 mL of water. The solvent was evaporated off at room temperature, dried in a vacuum oven at 110°C overnight, and calcined at 600°C for 1 hr. The impregnation procedure was repeated with the remaining Ni nitrate solution and again the impregnated monolith was dried in a vacuum oven at 110°C overnight and calcined at 600°C for 1 hr. RhCl<sub>3</sub> 3H<sub>2</sub>O (0.0394g) was dissolved in 2 drops of H<sub>2</sub>O and 1 mL of acetone and the solution was dripped onto the monolith. The solvents were evaporated at room temperature, dried in a vacuum oven at 110°C overnight, and calcined at 600°C for one hr. HRTEM and XAS analyses indicated that the catalyst was comprised of a Ni-Rh alloy.

**Test Procedure for Examples 11 and 12**

The partial oxidation reactions were done with a conventional flow apparatus using a 19 mm O.D. x 13 mm I.D. and 12" long quartz reactor. A ceramic foam of 99% Al<sub>2</sub>O<sub>3</sub> (12

mm OD x 5 mm of 45 ppi) were placed before and after the catalyst as radiation shields. The inlet radiation shield also aided in uniform distribution of the feed gases. An Inconel sheathed, single point K-type (Chromel/Alumel) thermocouple (TC) was placed axially inside the reactor touching the top (inlet) face of the radiation shield. A high temperature S-Type (Pt/Pt 10% Rh) bare-wire TC was positioned axially touching the bottom face of the catalyst and was used to indicate the reaction temperature. The catalyst and the two radiation shields were sealed tight against the walls of the quartz reactor by wrapping them radially with a high purity (99.5%) alumina paper. A 600 watt band heater set at 90% electrical output was placed around the quartz tube, providing heat to light off the reaction and to preheat the feed gases. The bottom of the band heater corresponded to the top of the upper radiation shield. In addition to the TCs placed above and below the catalyst, the reactor also contained two axially positioned, triple-point TCs, one before and another after the catalyst. These triple-point thermocouples were used to determine the temperature profiles of reactants and products subjected to preheating and quenching, respectively.

All runs were carried out at a CH<sub>4</sub>:O<sub>2</sub> molar ratio of 2:1 with a combined flow rate of 7.7 standard liters per minute (SLPM) (431,720 GHSV) and at a pressure of 5 psig (136 kPa). The reactor effluent was analyzed using a gas chromatograph equipped with a thermal conductivity detector. The C, H and O mass balance were all between 98% and 102%. Table 2 shows the results for the comparative set, with and without Rh. The inclusion of Rh in the catalyst composition resulted in higher CH<sub>4</sub> conversion and higher selectivities to CO and H<sub>2</sub> products.

Table 2

Ex.	Preheat Temp. °C	Catal. Temp. °C	% CH <sub>4</sub> / % O <sub>2</sub> Conv.	% CO / % H <sub>2</sub> Sel.	H <sub>2</sub> :CO
11	360	890	86 / 97	97 / 93	1.92
12	300	890	92 / 100	98 / 96	1.96

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit

and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims  
5 which follow, that scope including all equivalents of the subject matter of the claims. The disclosures of all patents and publications cited herein are incorporated by reference in their entirety.



## CLAIMS

What is claimed is:

- 5 1. A catalyst comprising about 1-50 weight percent nickel and about 0.01-10 weight percent rhodium, and a support structure, said catalyst having activity for catalyzing the production of  $H_2$  and CO in a molar ratio of about 2:1 from a reactant gas mixture comprising methane and  $O_2$  under partial oxidation promoting conditions of temperature, flowrate and feed composition in a millisecond contact time reactor.
- 10 2. The catalyst of claim 1 wherein said support structure comprises a substance chosen from the group consisting of spinels, perovskites, magnesium oxide, pyrochlores, brownmillerites, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet, alumina, cordierite,  $ZrO_2$ ,  $MgAl_2O_4$ ,  $SiO_2$  and  $TiO_2$ , said rhodium and  
15 nickel being disposed on said support structure.
3. The catalyst of claim 2 wherein said support structure comprises a substance chosen from the group consisting of spinels, perovskites, pyrochlores and brownmillerites, and said rhodium and said nickel being incorporated into said support structure.
4. The catalyst of claim 1 comprising a solid solution of rhodium-nickel-magnesium-  
20 oxide.
5. The catalyst of claim 2 wherein said substance is a refractory oxide.
6. The catalyst of claim 5 wherein said support structure comprises a foam structure.
7. The catalyst of claim 6 wherein said foam structure comprises about 12-60 pores per centimeter of structure.
- 25 8. The catalyst of claim 5 wherein said support structure comprises a honeycomb monolith structure.
9. The catalyst of claim 2 comprising 1% rhodium, 3% manganese and 13% nickel on a  $MgAl_2O_4$  support structure.
10. The catalyst of claim 2 comprising 1% rhodium and  $LaZr_{0.5}Ni_{0.5}O_3$ .
- 30 11. The catalyst of claim 2 comprising  $Rh_{0.02}Ni_{0.03}Mg_{0.95}O$ .
12. The catalyst of claim 2 comprising rhodium, nickel and cobalt on a support structure comprising  $ZrO_2$ .

13. The catalyst of claim 2 comprising rhodium and nickel on a support structure comprising  $\text{Al}_2\text{O}_3$ .

14. The catalyst of claim 2 comprising 1% rhodium, 10.9% nickel and 8.6% magnesium on a support structure comprising 99%  $\text{Al}_2\text{O}_3$ .

5 15. A process of preparing a product gas mixture comprising CO and  $\text{H}_2$  from a  $\text{C}_1\text{-C}_5$  hydrocarbon and  $\text{O}_2$ , the process comprising:

contacting a reactant gas mixture comprising said hydrocarbon and a source of molecular oxygen with a catalytically effective amount of a supported catalyst comprising about 1-50 weight percent nickel, about 0.01-10 weight percent rhodium, optionally, at least  
10 one metal chosen from the group consisting of lanthanide elements, zirconium, cobalt, manganese and magnesium, and a support structure; and

maintaining said supported catalyst and said reactant gas mixture at catalytic partial oxidation promoting conditions of temperature, gas flow rate and feed composition during said contacting.

15 16. The process of claim 15 wherein said support structure comprises a substance selected from the group consisting of spinels, perovskites, magnesium oxide, pyrochlores, brownmillerites, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet, alumina, cordierite,  $\text{ZrO}_2$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$ .

20 17. The process of claim 16 wherein said support structure comprises a substance chosen from the group consisting of spinels, perovskites, pyrochlores and brownmillerites, and said nickel and said rhodium are incorporated into said support structure.

18. The process of claim 15 wherein said support structure comprises a solid solution of rhodium-nickel-magnesium-oxide.

25 19. The process of claim 15 wherein said step of maintaining said catalyst and said reactant gas mixture at conversion promoting conditions of temperature, gas flow rate and feed composition during said contacting includes maintaining a temperature of about 600-1200°C.

30 20. The process of claim 19 wherein said step of maintaining a temperature includes maintaining a temperature of about 700-1100°C.

21. The process of claim 15 wherein said step of maintaining said catalyst and said reactant gas mixture at conversion promoting conditions of temperature, gas flow rate and

feed composition during said contacting includes maintaining a pressure of about 100-12,500 kPa.

22. The process of claim 21 wherein said step of maintaining a pressure includes maintaining a pressure of about 130-10,000 kPa.

5 23. The process of claim 15 further comprising mixing a methane-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1.

24. The process of claim 23 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 1.3:1 to about 2.2:1.

10 25. The process of claim 24 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 1.5:1 to about 2.2:1.

26. The process of claim 25 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 2:1.

15 27. The process of claim 23 wherein said oxygen-containing gas further comprises steam, CO<sub>2</sub>, or a combination thereof.

28. The process of claim 15 further comprising mixing a hydrocarbon feedstock and a gas comprising steam and/or CO<sub>2</sub> to provide said reactant gas mixture.

29. The process of claim 15 wherein said C<sub>1</sub>-C<sub>5</sub> hydrocarbon comprises at least about 50 % methane by volume.

20 30. The process of claim 29 wherein said C<sub>1</sub>-C<sub>5</sub> hydrocarbon comprises at least about 80 % methane by volume.

31. The process of claim 15 further comprising preheating said reactant gas mixture.

25 32. The process of claim 15 further comprising passing said reactant gas mixture over said catalyst at a space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h).

33. The process of claim 32 wherein said step of passing said reactant gas mixture over said catalyst comprises passing said mixture at a space velocity of about 50,000 to about 50,000,000 NL/kg/h.

30 34. The process of claim 15 wherein said step of contacting said supported catalyst and said reactant gas mixture includes maintaining a contact time of no more than about 10 milliseconds.

35. The process of claim 15 further comprising retaining said catalyst in a fixed bed reaction zone.

36. A process of converting a C<sub>1</sub>-C<sub>5</sub> hydrocarbon comprising at least about 50 vol% methane to a product gas mixture comprising CO and H<sub>2</sub> in a molar ratio of about 2:1, the process comprising:

5 mixing a methane-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1;

10 in a millisecond contact time reactor, contacting said reactant gas mixture feedstock with a catalytically effective amount of a supported catalyst comprising about 1-50 weight percent nickel, about 0.01-10 weight percent rhodium, optionally, at least one metal chosen from the group consisting of a lanthanide element, zirconium, cobalt, manganese and magnesium, and a support structure comprising a substance chosen from the group consisting of spinels, perovskites, pyrochlores and brownmillerites;

15 passing said reactant gas mixture feedstock over said catalyst at a space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h);

during said contacting, maintaining said supported catalyst and said reactant gas mixture at a temperature of about 600-1200°C; and

during said contacting, maintaining said supported catalyst and said reactant gas mixture at a pressure of about 100-12,500 kPa.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/28648

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/89 B01J23/46 B01J35/04 C01B3/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 040 066 A (IMPERIAL CHEMICAL INDUSTRIES LTD) page 1, line 57 - line 62 page 2, line 7-17 page 2, line 122 -page 3, line 3 page 3, line 70 - line 73 page 4, line 25 -page 5, line 3 page 12, line 13 - line 15 page 14, line 19 - line 21 ---	1-36
X	US 3 334 055 A (IMPERIAL CHEMICAL INDUSTRIES LTD) 1 August 1967 (1967-08-01) column 2, line 12 - line 21 column 2, line 49 - line 58 column 3, line 71 -column 4, line 21 column 5, line 10 - line 62 examples 1,2 --- -/--	1-36

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 744 419 A (CHOUDHARY VASANT RAMCHANDRA ET AL) 28 April 1998 (1998-04-28) column 6, line 46 - line 67 column 7, line 66 - column 8, line 18 claims 1,5,9,10</p> <p style="text-align: center;">---</p>	1-36
X	<p>US 5 039 510 A (PINTO ALWYN) 13 August 1991 (1991-08-13) column 1, line 9 - line 11 column 2, line 3 - column 3, line 2 column 4, line 29 - line 48 column 8, line 61 - line 67 column 9; table 1</p> <p style="text-align: center;">---</p>	1-36
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X	<p>US 3 953 363 A (YAMAUCHI SHIN ET AL) 27 April 1976 (1976-04-27) column 2, line 35 - line 47 Table 2-1 example 1 claims 1,5-9</p> <p style="text-align: center;">---</p>	1,2,5,6, 8,13
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