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(54) Title: CHROMIUM-BASED CATALYSTS AND PROCESS FOR CONVERTING HYDROCARBONS TO SYNTHESIS GAS

(57) Abstract: Processes and a new family of chromium-based catalysts for the catalytic conversion of hydrocarbons to carbon monoxide and hydrogen are disclosed. One highly active and selective catalyst system, providing greater than 95% CH_4 conversion, and 97-98 % selectivity to CO and H_2 at conversion-promoting conditions and high space velocity, is a chromium-containing catalyst consisting of a $CoCr_2O_4$ cubic spinel precursor dispersed in a chromium oxide matrix. The catalyst precursor is reduced to cobalt metal (in a chromium oxide matrix) in the reactant stream.

CHROMIUM-BASED CATALYSTS AND PROCESS FOR CONVERTING HYDROCARBONS TO SYNTHESIS GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Patent Application 60/163,843 filed November 5, 1999, the disclosure of which is incorporated by reference herein.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to catalysts and processes for the catalytic conversion of hydrocarbons (e.g., natural gas) using chromium-based catalysts to produce carbon monoxide and hydrogen. More particularly, the invention relates to such catalysts and their manner of making, and to processes employing the catalysts.

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 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 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 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.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (1)$$

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_2:CO ratio of 2:1, as shown in Equation 2.

$$CH_4 + 1/2O_2 \Leftrightarrow CO + 2H_2 \quad (2)$$

This ratio is more useful than the H_2: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 described in the art for the production of syngas via catalyzed partial oxidation reactions. The noble metals, which typically serve as the best catalysts for the partial oxidation of methane, are scarce and expensive. The widely used, less expensive, nickel-based catalysts have the disadvantage of promoting coke formation on the catalyst during the reaction, which results in loss of catalytic activity.

U.S. Pat. No. 5,149,516 discloses a process for the partial oxidation of methane comprising contacting methane and a source of oxygen with a perovskite of the formula ABO_3, where B can be a variety of metals including Cr. In the example shown, the perovskite that was used is $LaCoO_3$. M. Stojanovic et al., (*J. Catal.* (1997) 166 (2), 324-332) disclose the use of chromium-containing ternary perovskite oxides, $LaCr_{1-x}Ni_xO_3$ ($x = 0$ to 1.0) as catalysts for the partial oxidation of methane to syngas. The catalytic activity was found to increase monotonically with the value of x, i.e., $LaCrO_3$ was found to be the least active catalyst.

U.S. Pat. No. 5,447,705 also discloses a process for the partial oxidation of methane to syngas by contacting the starting materials with a catalyst having a perovskite crystalline structure and having the composition $Ln_xA_{1-y}B_yO_3$, in which x is a number such that $0<x<10$, y is a number such that $0<y<1$, Ln is at least one of a rare earth, strontium or bismuth, A is a metal of groups IVb, Vb, VIb, VIIb or VIII, A is a metal of groups IVb, Vb, VIb, VIIb or VIII and A and B are two different metals. Various combinations of La, Ni and Fe were exemplified.

[0010] 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, which is either: (a) a catalyst of the formula $M_xM'_yO_z$ where: M is at least one element selected from Mg, B, Al, Ln, Ga, Si, Ti, Zr and Hf; Ln is at least one member of lanthanum and the lanthanide series of elements, M' is a d-block transition metal, and each of the ratios x/z and y/z and $(x+y)/z$ is independently from 0.1 to 8; or (b) an oxide of a d-block transition metal; or (c) a d-block transition metal on a refractory support ; or (d) a catalyst formed by heating a) or b) under the conditions of the reaction or under non-oxidizing conditions. The d-block transition metals are selected from those having atomic number 21 to 29, 40 to 47 and 72 to 79, the metals Sc, Ti, Va, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Tc, Ru, Rh, Pa, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au. Preferably M' is selected from Fe, Os, Co, Rh, Ir, Pd, Pt and particularly Ni and Ru.

U.S. Pat. No. 5,431,855 describes a catalyst which catalyzes the combined partial oxidation-dry reforming reaction of a reactant gas mixture comprising CO_2, O_2 and CH_4 to for a product gas mixture comprising CO and H_2. Related patent U.S. Pat. No. 5,500,149 describes similar catalysts and methods for production of product gas mixtures comprising H_2 and CO.

U.S. Pat. No. 2,942,958 discloses an improved method for converting methane to carbon monoxide and hydrogen employing a reforming catalyst for the steam-methane reaction. Although it is stated that any reforming catalyst is suitable for the process, the preferred catalysts are nickel, chromium and cobalt, or their oxides.

U.S. Pat. No. 4,843,181 discloses a process for preparing Cr_2O_3 that includes pyrolysis of ammonium dichromate. The chromium oxide is employed in a process for manufacturing 1,1,1-trifluorodichloroethane and 1,1,1,2-tetrafluorochloroethane. U.S. Pat. No. 5,036,036 discloses an improved Cr_2O_3 catalyst composition, prepared by pyrolysis of ammonium dichromate, which is useful in hydrofluorination reactions.

An example of the previous attempts at synthesis gas production by catalytic partial oxidation to overcome some of the disadvantages and costs of steam reforming are described in EP303438 entitled "Production of Methanol from Hydrocarbonaceous Feedstock." The asserted advantages of EP303438 are relatively independent of catalyst composition, i.e., "partial oxidation reactions will be mass transfer controlled. Consequently, the reaction rate is relatively independent of catalyst activity, but dependent on surface area-to-volume ratio of the catalyst." A monolith catalyst is used with or without metal addition to the surface of the monolith at space velocities of 20,000-500,000 hr^{-1}. The suggested metal coatings of the monolith are selected from the exemplary list of palladium, platinum, rhodium, iridium, osmium, ruthenium, nickel, chromium, cobalt, cerium, lanthanum, and mixtures thereof in addition to metals of the groups IA, IIA, III, IV, VB, VIB, or VIIB. An exemplary catalyst comprises alumina on cordierite, with a coating comprising platinum and palladium. Steam is required in the feed mixture to suppress coke formation on the catalyst. Products from the partial oxidation of methane employing these catalysts results in the production of significant quantities of carbon dioxide, steam, and C_2+ hydrocarbons.

None of the prior art processes or catalysts describes a completely satisfactory catalyst or process capable of high conversion and high selectivity for CO and H_2 products and which are capable of operation with very low coke formation. Accordingly, there remains a need for a process and catalyst for converting hydrocarbons, particularly methane, that have low coke formation, high conversions of methane and high selectivities to CO and H_2, and which are economically feasible at commercial-scale conditions.

SUMMARY OF THE INVENTION

Many of the shortcomings of conventional syngas manufacturing methods are overcome by the processes and catalysts of the present invention. The preferred chromium-based catalysts provide high levels of activity (i.e., conversion of CH_4) and high selectivity to CO and H_2 reaction products than is typically available with conventional catalytic systems designed for commercial-scale use. Another advantage of the catalytic compositions and syngas production processes of the invention is that no appreciable coking occurs with use of many of the chromium-containing catalyst compositions. Still another advantage of the new catalysts and processes is that they are more economically feasible for use in commercial-scale conditions than conventional catalysts now used for producing syngas. Some catalyst compositions containing higher-melting-point pure ceramic oxides instead of metals, demonstrate improved catalyst life when used for production of syngas.

In accordance with one aspect of the invention, a process for the catalytic conversion of a hydrocarbon feedstock to syngas is provided. Conversion of the hydrocarbon is achieved by contacting a feed stream comprising the hydrocarbon feedstock and an oxygen-containing gas with a chromium-based catalyst in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising carbon monoxide and hydrogen. In accordance with another aspect of the invention is provided catalyst compositions comprising a chromium-containing compound optionally combined with at least one metal selected from the group consisting of Group 1, Group 2, Group 11 and Group 12 of the periodic table of the elements; a metal with an atomic number of 57 through 71; Co, Ru, Rh, Pd, Ir, Pt, Al, Ti, Y and Zr, and optionally Si. The preferred compositions do not have a perovskite structure. Yet another aspect of the present invention includes methods of making the new chromium-based catalytic compositions.

As discussed in more detail below, many of the new chromium-based catalysts exhibit high methane oxidation activities and selectivities to syngas (CO and H_2) in a millisecond contact time reactor. The low light-off temperatures of these materials (i.e., less than 650°C) and superior performance are indicative of the more preferred catalytic compositions. Pure chromium oxide catalysts, and chromium catalysts containing rare earth oxides show little or no carbon or coke build-up after reaction with CH_4/O_2. Trends in light-off temperature appear to correlate with the basicity or ionicity of the rare earth components, which may, in turn, relate to trends in C-H activation. Chromium oxide-based catalysts containing cobalt show carbon deposition on the reduced cobalt metal particles which are formed *in situ*.

In accordance with certain embodiments of the present invention, a chromium-based composition for catalyzing the conversion of a C_1-C_5 hydrocarbon to form a product gas mixture containing CO and H_2 is provided. The composition comprises about 0.1-100 mole % of chromium or chromium-containing compound per total moles of metal or metal ion in the composition. The composition also includes at least one other elemental metal or metal-containing compound, the metal of which is Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Zn, Cd, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Ni, Ru or Rh. Optionally, the composition may also contain an oxidatively and thermally stable porous support. The chromium-based composition does not have a perovskite structure, however. In certain embodiments which include a porous material, or support, the porous material may include at least one oxide or oxyhydroxide of a metal such as magnesium, silicon, titanium, tantalum, zirconium or aluminum.

In some embodiments of the catalyst compositions the chromium or chromium-containing compound comprises about 10-100 mole % of the total moles of metal or metal ion in said composition. . In some embodiments the catalyst composition initially comprises a catalyst precursor comprising a metal and a metal oxide, and after reaction in a syngas reactor, the catalyst finally comprises reduced metal and metal oxide. In some of these embodiments, the catalyst precursor comprises $CoCr_2O_4$, the reduced metal is zero valent cobalt metal, and the metal oxide is Cr_2O_3. Some of these compositions finally comprise, after exposure to reaction conditions for a period of time, metal oxide and substantially no deposited carbon.

In some embodiments, the composition comprises a matrix structure which is a xerogel or an aerogel. In some embodiments the matrix structure comprises at least one oxide or oxyhydroxide of a metal such as magnesium, silicon, titanium, tantalum, zirconium or aluminum. Certain chromium-based compositions of the invention have a matrix structure comprising at least 30 wt %, preferably about 30-99.9 mole %, and more preferably about 50-97.5 mole % of the total moles (of metal) of the composition. In some embodiments the matrix structure comprises titanium oxide/oxyhydroxide, or magnesium oxide/oxyhydroxide and silicon oxide/oxyhydroxide. In some embodiments the chromium-based composition also contains cobalt or a cobalt-containing compound. In some embodiments, the composition also includes lanthanum or a lanthanum-containing compound. Certain catalytic chromium-based compositions contain magnesium or a magnesium-containing compound and silicon oxide/oxyhydroxide. In certain embodiments, the chromium-based composition contains cerium or samarium, or compounds containing those metals. There are some embodiments that include gold and aluminum oxide/oxyhydroxide, in addition to chromium or a chromium-containing compound. In other embodiments, the chromium-based catalytic composition comprises gold or a gold-containing compound and magnesium oxide/oxyhydroxide. Still other embodiments contain lanthanum and lithium, or compounds containing those elements, and α-Al_2O_3, in addition to chromium or a chromium-containing compound.

Some embodiments of the chromium-based catalytic compositions comprise a catalyst support, which may be oxidatively and thermally stable. The catalyst support may also be in the form of a porous three-dimensional monolith or it could be a reticulated ceramic or ceramic foam.

In accordance with another aspect of the invention, a process in provided for preparing a chromium-based composition for catalyzing the partial oxidation of a C_1-C_5 hydrocarbon to form a product gas mixture comprising CO and H_2. This process comprises combining about 0.1-100 mole % elemental chromium or chromium-containing compound per total moles of metal in the composition, together with, optionally, at least one other metal or metal oxide the metal component of which is Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Zn, Cd, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Ni, Ru or Rh. Optionally the composition also contains at least one matrix-forming material such as an alkoxide of magnesium, silicon, titanium, tantalum, zirconium or aluminum. The process also includes forming the combination into a porous solid. The matrix-forming material may be at least 30 wt % of the total weight of said composition with said chromium compound and said at least one other metal compound. In some embodiments the matrix-forming material comprises titanium or titanium oxide, or a combination of oxides or alkoxides of magnesium and silicon.

In some embodiments, the process also includes preparing an intermediate composition containing the chromium or chromium-containing compound and at least one other metal or metal-containing compound. In this embodiment, the process includes applying the intermediate composition to a porous matrix material comprising at least 30 wt % of the total weight of the composition. The porous matrix material may comprise a porous monolith support and the intermediate composition may be in the form of a liquid which is applied to the porous matrix material by impregnation. In some embodiments, the intermediate composition is dried, or calcined. Certain embodiments of the process provide for calcining the composition *in situ* under reaction conditions. In some embodiments the composition is formed by freeze-drying, spray drying or spray roasting the intermediate composition. In some embodiments, a powder is formed, which may be compressed into a pellet. Other embodiments of the process for making a chromium-based catalyst composition include forming an extrudate, or a gel such as a xerogel or aerogel.

In some embodiments, the process of making a chromium-based catalytic composition employs a matrix-forming material comprising at least one metal alkoxide. The metal alkoxide may contain 1 to 20 carbon atoms, and in some embodiments contains 1 to 5 carbon atoms. Some embodiments combine with the chromium or chromium-containing compound at least one metal alkoxide that is a C_1-C_4 alkoxide such as tantalum n-butoxide, titanium isopropoxide or zirconium isopropoxide. In certain embodiments of the process of making the chromium-based catalyst composition, the process includes dissolving at least one of the metal alkoxides in a non-aqueous medium to form a metal alkoxide solution. In some of these embodiments, the metal alkoxide solution is mixed with a protic solvent, such as water, whereby the alkoxide(s) react(s) with the protic solvent to form a gel. Some embodiments include first dissolving the chromium or chromium-containing compound in the protic solvent to form a protic catalytic metal solution. In some alternative embodiments, the process may include dissolving or suspending the matrix material in the non-aqueous liquid medium to form a non-aqueous matrix solution or colloidal suspension. In some embodiments, the process may include dissolving at least one other elemental metal or metal-containing compound and one or more matrix-forming component in a non-aqueous medium.

Certain embodiments of the process for making a chromium-based catalytic composition provide for combining a protic solvent and an alkoxide in a molar ratio of about 5:1 to 53.1 or about 26.5:1. The process may include the gradual addition and mixing of sufficient protic solution to induce hydrolysis and condensation of the metal alkoxide(s). In certain embodiments the mixing comprises combining water and the alkoxide in a molar ratio of about 0.1:1 to 10:1 water:alkoxide. Some embodiments include combining water and zirconium alkoxide or titanium alkoxide in a molar ratio of about 4:1.

In accordance with yet another aspect of the present invention, processes are provided for converting a C_1-C_5 hydrocarbon to form a product gas mixture containing CO and H_2. In certain embodiments the process comprises mixing a C_1-C_5 hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock. The process includes contacting said reactant gas mixture feedstock with a catalytically effective amount of one of the above-described chromium-based catalyst compositions. During the catalyst/reactant gas contacting period, the composition and the reactant gas mixture are maintained at a temperature of about 600-1,100°C or about 700-1,000°C. The catalyst composition/reactant gas system is also maintained at a pressure of about 100-12,500 kPa, preferably about 130-10,000 kPa, and the reactant gas mixture is passed over the catalyst composition at a continuous flow rate of about 2,000 to about 10,000,000 NL/kg/h, preferably about 5,000 - 5,000,000 NL/kg/h. Some embodiments of the syngas manufacturing process include mixing a methane-containing gas feedstock and an oxygen-containing gas feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1, or about 1.3:1 to about 2.2:1, or about 1.5:1 to about 2.2:1, preferably about 2:1.

In some embodiments of the hydrocarbon conversion processes, the oxygen-containing gas further comprises steam, CO_2, or a combination thereof. In some embodiments the process comprises mixing a hydrocarbon feedstock and a gas comprising steam and/or CO_2 to provide a reactant gas mixture. In some embodiments the C_1-C_5 hydrocarbon comprises at least about 50 % methane by volume of the reactant gas mixture, preferably at least about 75 %, and more preferably at least about 80 % methane by volume of the reactant gas mixture. Certain embodiments of the processes of making syngas provide for preheating the hydrocarbon feedstock and the oxygen-containing feedstock before contacting the catalyst composition. In some embodiments the catalyst composition in a fixed bed reaction zone.

One embodiment of the process of converting a hydrocarbon to methane and hydrogen employs a particularly highly active and selective catalyst system. This process includes mixing a C_1-C_5 hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock. The reactant gas mixture feedstock is contacted with a catalytically effective amount of a $CoCr_2O_4$ cubic spinel precursor dispersed in a chromium oxide matrix. During this contacting, the catalyst composition and the reactant gas mixture are maintained at a temperature of about 600-1,100°C. and at a pressure of about 100-12,500 kPa. The reactant gas mixture is passed over the catalyst composition at a continuous flow rate of about 2,000 to about 10,000,000 NL/kg/h. The catalyst precursor is reduced to cobalt metal (in a chromium oxide matrix) in the reactant stream. This process achieves greater than 95 % CH_4 conversion of the hydrocarbon in the reactant gas mixture, and achieves at least about 97-98 % selectivity to CO and H_2.

Certain embodiments provide a process for converting a C_1-C_5 hydrocarbon that contains at least about 80 vol% methane to form a product gas mixture comprising CO and H_2. This process may include mixing a methane-containing gaseous feedstock and an oxygen-containing gaseous feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1. The gaseous feedstocks are preheated and combined, and the reactant gas mixture feedstock is then contacted with a catalytically effective amount of a chromium-based composition containing about 10-100 mole % (as the metal) chromium or chromium-containing compound per total moles of metal or metal ion in the catalyst composition. The catalyst composition also contains 0-90% cobalt or cobalt-containing compound, and optionally, an oxidatively and thermally stable porous support supporting the chromium or chromium-containing compound and the cobalt or cobalt-containing compound. The catalyst composition comprises a structure other than a perovskite structure. During the gas/catalyst contacting period, the composition and reactant gas mixture are maintained at a temperature of about 600-1,100°C and at a pressure of about 100-12,500 kPa. The reactant gas mixture is passed over the catalytic composition at a continuous flow rate of about 2,000 to 10,000,000 NL/kg/h.

In some embodiments of the syngas manufacturing methods the catalytic composition is nominally 0.8 mole % in elemental chromium or chromium ion and 0.2 mole % in elemental cobalt or cobalt ion. In other embodiments the composition is nominally 0.2 mole % in elemental chromium or chromium ion and 0.8 mole % in elemental cobalt or cobalt ion. In still other embodiments the composition is nominally 0.5 mole % in elemental chromium or chromium ion and 0.5 mole % in elemental cobalt or cobalt ion.

Certain embodiments of the processes for converting a hydrocarbon to yield CO and H_2 employ a catalytic composition that is nominally 2-10 mole % chromium or chromium ion, 1 mole % in lithium or lithium ion and 27 mole % lanthanum or lanthanum ion and also includes an α-AlO_3 support. Such processes also provide at least 90% conversion of CH_4 and at least 90% selectivities for CO and H_2 products. Other embodiments, features and advantages of the present invention will become apparent with reference to the following figures and description.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a bar graph comparing the catalyst performance of three pure chromium oxide systems. The black bars indicate the % CH_4 conversion and the cross-hatched bars indicate the % CO selectivity.

Fig. 2A is a transmission electron microscopy photomicrograph showing the crystal structure of a representative freeze-dried chromium oxide catalyst as prepared.

Fig. 2B is similar to **Fig. 2A** but was taken after the catalyst was employed 6 hours on stream

Fig. 3 is a graph showing trends in light-off temperature and basicity/ionicity of representative "support" matrix compositions.

Fig. 4 is a graph showing the results of thermal gravimetric analysis (TGA) studies of a representative rare earth oxide based chromium catalyst.

Fig. 5 is a graph showing the reaction chemistry for several representative ternary freeze dried chromium oxides containing chromium and cobalt.

Fig. 6A is X-ray diffraction data for the catalyst precursor $Co_{0.2}Cr_{0.8}Ox$ following reaction *in situ* (i.e., on stream).

Fig. 6B is like **Fig. 6A,** except the catalyst specimen was taken before reactor evaluation.

Fig. 7 A shows the X-ray diffraction data for $Co_{0.2}Cr_{0.8}Ox$ after reactor evaluation.

Fig. 7 B shows the X-ray diffraction data for $Co_{0.5}$ $Cr_{0.8}Ox$ after reactor evaluation.

Fig. 7 C shows the X-ray diffraction data for $Co_{0.8}$ $Cr_{0.2}Ox$ after reactor evaluation.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Catalyst Preparation

The chromium-containing catalysts useful for catalyzing the partial oxidation of methane to CO and H_2 are prepared by employing a variety of known art techniques such as impregnation, xerogel or aerogel formation, freeze-drying, spray drying, and spray roasting. In addition to catalyst powders, extrudates and pellets, monoliths can be used as supports provided that they have sufficient porosity for reactor use. The supports used with some of the catalyst compositions may be in the form of monolithic supports 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 in, for example, *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"). Additionally, some of the preferred three-dimensional forms of these new catalysts include chromium oxide reticulated ceramics or ceramic foams, and directly deposited materials on three-dimensional monoliths, which are needed for millisecond contact time reactors and for commercial use. The impregnation techniques preferably comprise contacting the support with a solution of a compound of the catalytically active material, or a solution of compounds of the catalytically active materials or their precursors. The contacting is followed by drying and calcining, or transforming or thermally treating the supported materials under reaction conditions; in some cases this thermal treatment can be accomplished *in situ* under reaction conditions.

A key component of the most preferred catalysts is chromium, and optionally at least one other metal selected from the group consisting of Group 1 (i.e., Li, Na, K, Rb and Cs); Group 2 (i.e., Mg, Ca, Sr and Ba); Group 11 (i.e., Cu, Ag and Au); Group 12 (i.e., Zn and Cd); metals with atomic numbers of 57 through 71 (i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), Co, Ni, Ru and Rh. The catalyst, or catalytic composition, must contain a catalytically effective amount of the metal component(s). The amount of catalytic metal present in the composition may vary widely. Preferably the catalyst comprises from about 0.1 mole % to about 100 mole % (as the metal) of chromium per total moles of catalytic metal and matrix metal, and more preferably from about 10 mole % to about 100 mole %. A matrix is a skeletal framework of oxides and oxyhydroxides. One or more of the catalytic components may also serve as a matrix material in which another catalytic metal or metal-containing compound is dispersed. For example, a catalyst composition may include a $CoCr_2O_4$ cubic spinel catalyst precursor dispersed in a chromium oxide matrix. This catalyst precursor is then reduced to cobalt metal in a chromium oxide matrix by the hot gases of the reactant stream. A suitable matrix can also be obtained from the hydrolysis and condensation of alkoxides and/or other reagents. Alternatively, or additionally, an oxidatively and thermally stable material may serve as a matrix or a support for the catalyst composition. For example, a composition containing 10% Cr, 1% Li, 27% La and α-Al_2O_3 may be used.

Xerogels and Aerogels from Metal Alkoxides

For the purposes of this disclosure, the term “gel” refers to a coherent, rigid three-dimensional polymeric network. As described in more detail below, the present gels are formed in a liquid medium, usually water, alcohol, or a mixture thereof. The term "alcogel" refers to gels in which the pores are filled with predominantly alcohol. Gels whose pores are filled primarily with water may be referred to as aquagels or hydrogels. A "xerogel" is a gel from which the liquid medium has been removed and replaced by a gas. In general, the structure is compressed and the porosity reduced significantly by the surface tension forces that occur as the liquid is removed. As soon as liquid begins to evaporate from a gel at temperatures below the critical temperature, surface tension creates concave menisci in the gel's pores. As evaporation continues, the menisci retreat into the gel body, compressive forces build up around its perimeter, and the perimeter contracts, drawing the gel body inward. Eventually surface tension causes significant collapse of the gel body and a reduction of volume, often as much as two-thirds or more of the original volume. This shrinkage causes a significant reduction in the porosity, often as much as 90 to 95 percent depending on the system and pore sizes.

In contrast to a xerogel, an "aerogel" is a gel from which the liquid has been removed in such a way as to prevent significant collapse or change in the structure as liquid is removed. This is typically accomplished by heating the liquid-filled gel in an autoclave while maintaining the prevailing pressure above the vapor pressure of the liquid until the critical temperature of the liquid has been exceeded, and then gradually releasing the vapor, usually by gradually reducing the pressure either incrementally or continuously, while maintaining the temperature above the critical temperature. The critical temperature is the temperature above which it is impossible to liquefy a gas, regardless of how much pressure is applied. At temperatures above the critical temperature, the distinction between liquid and gas phases disappears and so do the physical manifestations of the gas/liquid interface. In the absence of an interface between liquid and gas phases, there is no surface tension and hence no surface tension forces to collapse the gel. Such a process may be termed "supercritical drying." Aerogels produced by supercritical drying typically have high porosities, on the order of from 50 to 99 percent by volume.

The new xerogels or aerogels preferably comprise a matrix material that is essentially derived from a solution of one or more matrix components and incorporate the active catalyst component(s). The active catalyst components are preferably derived from one or more dissolved component. The matrix is a skeletal framework of oxides and oxyhydroxides derived from the hydrolysis and condensation of alkoxides and/or other reagents. This framework preferably comprises 30% or more, by weight, of the total catalyst composition. The matrix material comprises magnesium, silicon, titanium, zirconium or aluminum, oxide/hydroxide xerogels or aerogels, or mixtures thereof, totaling from 30 to 99.9 mole %, preferably 50-97.5 mole% of the catalyst composition. Especially preferred are combinations where the matrix metal is Ti and combinations where the matrix metal is a combination of Mg and Si.

In preparing a chromium-based catalyst, one or more metal alkoxides (e.g., titanium n-butoxide) may be used as starting material for preparing the gels. Suitable metal alkoxides are any alkoxide that contains from 1 to 20 carbon atoms, preferably 1 to 5 carbon atoms, in the alkoxide group. It is also preferred that the alkoxide is soluble in the liquid reaction medium. C_1-C_4 alkoxides such as tantalum n-butoxide, titanium isopropoxide and zirconium isopropoxide are especially preferred. Commercially available alkoxides can be used, if desired. In addition, suitable alkoxides can be prepared by other routes. Some examples include direct reaction of zero valent metals with alcohols in the presence of a catalyst. Many alkoxides can be formed by reaction of metal halides with alcohols. Alkoxy derivatives can be synthesized by the reaction of the alkoxide with alcohol in a ligand interchange reaction. Direct reactions of metal dialkylamides with alcohol also form alkoxide derivatives. Additional examples are disclosed in "Metal Alkoxides" by D.C. Bradley et al., Academic Press, (1978).

The first step in the synthesis of the gels containing alcohol, or alcogels, consists of first preparing non-aqueous solutions of the alkoxides and other reagents and separate solutions containing protic solvents such as water. When the alkoxide solutions are mixed with the solutions containing the protic solvents, the alkoxides will react and polymerize to form a gel.

The medium utilized in the process generally should be a solvent for the alkoxide or alkoxides which are utilized and the additional metal reagents and promoters which are added in the single step synthesis. Solubility of all components in their respective media (aqueous and non-aqueous) is preferred to produce highly dispersed materials. By employing soluble reagents in this manner, mixing and dispersion of the active metals and promoter reagents can be near atomic, in fact mirroring their dispersion in their respective solutions. The precursor gel thus produced by this process will contain highly dispersed active metals and promoters. High dispersion results in catalyst metal particles in the nanometer size range.

It is preferred that the catalytic metal component of the gel is dissolved in a separate protic solvent (e.g., water) and this solution of catalytic metal compound(s) is then mixed with the non-aqueous solution of the matrix component(s). Alternatively, the catalytic metal component is dissolved in the same non-aqueous solution as the matrix component(s), and an aqueous supplement is used.

The concentration or amount of solvent used is linked to the alkoxide content. A molar ratio of 26.5:1 ethanol:total alkoxide can be used, although the molar ratio of ethanol:total alkoxide can be from about 5:1 to 53:1, or even greater. If a large excess of alcohol is used, gelation will not generally occur immediately; some solvent evaporation will be needed. At lower solvent concentrations, it is thought by the inventors that a heavier gel will be formed having less pore volume and surface area.

The process continues with adding to the alcohol soluble alkoxide and other reagents, water and any aqueous solutions, in a dropwise fashion, to induce hydrolysis and condensation reaction. Depending on the alkoxide system, a discernible gel point can be reached in minutes or hours. The molar ratio of the total water added to total Mg, Si, Ti, Zr, and Al added (including water present in aqueous solutions) varies according to the specific alkoxide being reacted. Preferably, a molar ratio of water:alkoxide from about 0.1:1 to 10:1 is used. However, ratios close to 4:1 for zirconium(alkoxide)$_4$ and titanium(alkoxides)$_4$ can also be used with success. The amount of water utilized in the reaction is that calculated to hydrolyze the alkoxide in the reaction mixture. A ratio lower than that needed to hydrolyze the alkoxide species will result in a partially hydrolyzed material, which in most cases will reach a gel point at a much slower rate, depending on the aging procedure and the presence of atmospheric moisture.

The addition of acidic or basic reagents to the alkoxide medium can have an effect on the kinetics of the hydrolysis and condensation reactions, and the microstructure of the oxide/hydroxide matrices derived from the alkoxide precursor which entraps or incorporates the soluble metal and promoter reagents. It is preferred that a pH within the range of from 1 to 12 is used, with a pH range of from 1 to 6 being more preferred.

After reacting to form an alcogel, as described above, it may be necessary to complete the gelation process with some aging of the gel. This aging can range from one minute to several days. Generally, the alcogels are aged at room temperature in air for at least several hours.

Removal of solvent from the alcogels is accomplished by several methods. Removal by vacuum drying or heating in air results in the formation of a xerogel. An aerogel of the material can typically be formed by charging in a pressurized system such as an autoclave. The solvent-containing gel is placed in an autoclave where it can be contacted with a fluid above its critical temperature and pressure by allowing supercritical fluid to flow through the gel material until the solvent is no longer being extracted by the supercritical fluid. In performing this extraction to produce an aerogel material, various fluids can be utilized at their critical temperature and pressure. For instance, fluorochlorocarbons typified by Freon® fluorochloromethanes (e.g., Freon® 11 (CCl_3F), 12 (CCl_2F_2) or 114 ($CClF_2CClF_2$), ammonia and carbon dioxide are all suitable for this process. Typically, the extraction fluids are gases at atmospheric conditions, so that pore collapse due to the capillary forces at the liquid/solid interface are avoided during drying. The resulting material should, in most cases, possess a higher surface area than the non-supercritically dried materials.

The xerogels and aerogels thus produced may be described as precursor salts dispersed in an oxide or oxyhydroxide matrix. The hydroxyl content is at this point undefined; a theoretical maximum corresponds to the valence of central metal atom. The molar H_2O:alkoxide ratio can also impact the final xerogel stoichiometry so that there will be residual -OR groups in the unaged gel. However, reaction with atmospheric moisture will convert these to the corresponding -OH, and -O groups upon continued polymerization and dehydration. Aging, even under inert conditions, can also effect the condensation of the -OH, eliminating H_2O, through continuation of cross linking and polymerization, i.e., gel formation.

Xerogels and Aerogels from Inorganic Metal Colloids

Alternatively, one or more inorganic metal colloids may be used as starting material for preparing the gels. These colloids include colloidal alumina sols, colloidal ceria sols, colloidal zirconia sols or their mixtures. The colloidal sols are commercially available from well-known suppliers. There are also several methods of preparing colloids, as described in "Inorganic Colloid Chemistry", Volumes 1, 2 and 3, J. Wiley and Sons, Inc., 1935. Colloid formation involves either nucleation and growth, or subdivision or dispersion processes. For example, hydrous titanium dioxide sols can be prepared by adding ammonia hydroxide to a solution of a tetravalent titanium salt, followed by peptization (re-dispersion) by dilute alkalis. Zirconium oxide sol can be prepared by dialysis of sodium oxychlorides. Cerium oxide sol can be prepared by dialysis of a solution of ceric ammonium nitrate.

Commercially available alkoxides, such as tetraethylorthosilicate and Tyzor® organic titanate esters, may be used. However, alkoxides may also be prepared by various well-known routes. Examples include direct reaction of zero valent metal with alcohols in the presence of a suitable catalyst; and the reaction of metal halides with alcohols. Alkoxy derivatives can be synthesized by the reaction of the alkoxide with alcohol in a ligand interchange reaction. Direct reactions of metal dialkamides with alcohol also form alkoxide derivatives. Additional examples are described in D. C. Bradley et al., “Metal Alkoxides” (Academic Press, 1978).

In one especially preferred method of preparing a chromium-based catalyst, pre-formed colloidal sols in water, or aquasols, are used. The aquasols are comprised of colloidal particles ranging in size from 2 to 50 nanometers. In general, the smaller primary particle sizes (2 to 5 nm) are preferred. The pre-formed colloids contain from 10 to 35 weight % of colloidal oxides or other materials, depending on the method of stabilization. Generally, after addition of the active (for the partial oxidation reactions, either as a catalyst or promoter) metal components, the final de-stabilized colloids can possess from about 1 to 35 weight % solids, preferably from about 1 to 20 weight percent.

The colloidal oxides or their mixtures are destabilized during the addition of soluble salts of the primary and promoter cation species by the addition of acids or bases or by solvent removal, both of which alter pH. These changes modify the colloidal particle's electrical double layer. Each colloidal particle possesses a double layer when suspended in a liquid medium. For instance, a negatively charged colloid causes some of the positive ions to form a firmly attached layer around the surface of a colloid. Additional positive ions are still attracted by the negative colloid, but now they are repelled by the primary positive layer as well as the positive ions, and form a diffuse layer of counterions. The primary layer and the diffuse layer are referred to as the double layer. The tendencies of a colloid to either agglomerate (flocculate and precipitate) or polymerize when destabilized will depend on the properties of this double layer. The double layer, and resulting electrostatic forces can be modified by altering the ionic environment, or pH, liquid concentration, or by adding a surface active material directly to affect the charge of the colloid.

Once the particles come in close enough contact when destabilized, polymerization and crosslinking reaction between surface functional groups, such as surface hydroxyls, can occur. In this invention, the colloids, which are originally stable heterogeneous dispersions of oxides and other species in solvents, are destabilized to produce colloidal gels. Destabilization is induced, in some cases, by the addition of soluble salts, e.g., chlorides or nitrates, which change the pH and the ionic strength of the colloidal suspensions; by the addition of acids or bases; or by solvent removal. pH changes generally accompany the addition of soluble salts; in general, this is preferred over solvent removal. Generally, a pH range of from about 0 to about 12 can be used to destabilize the colloids; however, very large extremes in pH (such as pH 12) can cause flocculation and precipitation. For this reason, a pH range of from about 2 to 8 is preferred.

The medium utilized in this process is typically aqueous, although non-aqueous colloids can also be used. The additional metal or inorganic reagents (i.e., salts of Cr or promoters) used should be soluble in the appropriate aqueous and non-aqueous media.

Freeze Drying to Form the Solid Catalyst Composition

Removal of solvent from the gels can be accomplished by several methods as described above to prepare either an aerogel or xerogel. Freeze drying procedures can accommodate several catalyst compositions, and are useful if the catalyst precursors are soluble in water or other solvent which can be rapidly (<1 minute) frozen. Precursor salts are dissolved in an appropriate amount of solvent to form a solution or fine colloid. The solution is then rapidly cooled and frozen by immersion in a suitable medium, such as liquid nitrogen. If the solution is rapidly frozen, the salts and other components will remain intimately mixed and will not segregate to any significant degree. The frozen solid is transferred to a freeze drying chamber. The solution is kept frozen while water vapor is removed by evacuation. In the present studies, a two section Virtis freeze drying unit was employed. Refrigerated shelves were used to prevent thaw-out of the frozen solids during evacuation.

Spray Drying to Form the Solid Catalyst Composition

Spray drying procedures involve the use of solutions, colloids or slurries containing catalyst precursors or catalyst compounds. The technique consists of atomization of these liquids (usually but not exclusively aqueous) into a spray, and contact between spray and drying medium (usually hot air) resulting in moisture evaporation. The drying of the spray proceeds until the desired moisture content in the dried particles is obtained, and the product is recovered by suitable separation techniques (usually cyclone separation). A detailed description of spray drying methods can be found in "Spray Drying Handbook", 4th edition by K Masters (Longman Scientific and Technical, John Wiley and Sons, N.Y) c. 1985.

Spray Roasting to Form the Solid Catalyst Composition

Spray roasting also involves the use of solutions or colloids, but generally involves drying and calcination (at higher temperatures) in one process step to produce catalyst powders. Suitable spray roasting techniques are described in U.S. Pat. No. 5,707,910.

EXAMPLES

The catalyst compositions are given in atomic ratios except where otherwise noted.

Example 1: Cr(0.1)/La(0.9)

An aqueous solution of $Cr_3(OH)_2(CH_3CO_2)_7$ (2.22 mL, 2.5603 M in Cr) and aqueous $La(NO_3)_3$ (42.78 mL, 1.1955 M) were simultaneously added to a 150 mL petri dish with gentle swirling. The entire solution was rapidly frozen with liquid nitrogen and dried as a frozen solid under vacuum for several days to produce a freeze dried powder. The freeze dried material was heated in air at 350°C for.5 hours prior to pelletization and use. The final catalyst had a nominal composition of Cr(0.1)/La(0.9).

Example 2: Cr(0.025)/Mg(0.975)

A magnesium methoxide solution (68.767 mL, 0.3495 M) diluted with 50 volume % ethanol (punctilious) was added to a 150 mL petri dish with gentle swirling under an inert N_2 atmosphere. In a subsequent addition, aqueous $Cr_3(OH)_2(CH_3CO_2)_7$ solution (1.233 mL, 0.5 M in Cr) was introduced to the petri dish while it was gently swirled. Following the addition of the aqueous solutions, a gel point was realized and a homogeneous gel formed which was nearly white in color. The gel was allowed to age 8 days in air and then dried under vacuum at 120°C prior to use. The final xerogel had a nominal composition of Cr(0.025)/Mg(0.975).

Example 3: Cr(0.2)/Mg(0.4)/Si(0.4)

A magnesium methoxide solution (57.474 mL, 0.669 M) and a tetraethylorthosilicate (TEOS) solution (diluted with ethanol to 60 volume % TEOS, 40 volume % ethanol) were simultaneously added to a 150 mL petri dish with gentle swirling under a nitrogen atmosphere. In a subsequent step, aqueous $Cr_3(OH)_2(CH_3CO_2)_7$ solution (7.846 mL, 2.5603 M) was added. A white gel formed, and was aged for 5 days, dried under vacuum at 120°C for 5 hours prior to use. The final xerogel had a nominal composition of Cr(0.2)/Mg(0.4)/Si(0.4).

Example 4: Cr(0.1)/Ce(0.9)

An aqueous solution of $Cr_3(OH)_2(CH_3CO_2)_7$ (1.375 mL, 2.560 M in Cr) and aqueous solution of $Ce(NO_3)_3 \bullet 6H_2O$ (43.625 mL, 0.7261 M) were simultaneously added to a 150 mL pyrex petri dish with gentle swirling. The entire solution was rapidly frozen with liquid nitrogen and dried as a frozen solid under vacuum for several days to produce a freeze dried powder. The freeze dried material was heated in air at 350°C for 5 hours prior to pelletization and use. The final catalyst had a nominal composition of Cr(0.1)/Ce(0.9).

Example 5: Cr(0.1)/Sm(0.9)

An aqueous solution of $Cr_3(OH)_2(CH_3CO_2)_7$ (0.969 mL, 2.560 M in Cr) and an aqueous solution of samarium nitrate (44.031 mL, 0.5069 M), the solution was formed using water and nitric acid to bring the final pH to 0.24 to dissolve $Sm(NO_3)_3 \bullet 6H_2O$, were simultaneously added to a 150 mL pyrex petri dish with gentle swirling. The entire solution was rapidly frozen with liquid nitrogen and dried as a frozen solid under vacuum for several days to produce a freeze dried powder. The freeze dried material was heated in air at 350°C for 5 hours prior to pelletization and use. The final catalyst had a nominal composition of Cr(0.1)/Sm(0.9).

Example 6: Cr(0.1)/Co(0.25)/Ti(0.5)

A titanium n-butoxide solution in ethanol (2.67 mL, 60 volume %) was added to a 150 mL petri dish under an inert nitrogen atmosphere with gentle swirling. In a second step, an ethanolic solution of anhydrous $CoCl_2$ (2.342 mL, 1.00 M), glacial acetic acid (0.140 mL), H_2O (1.182 mL) and an ethanolic solution of chromium (III) acetylacetonate (93.667 mL, 0.03 M) were simultaneously added. A gel point was realized following the addition of the aqueous reagents, and the red, opaque gel which formed and was aged for at least 24 hours prior to drying under vacuum at 120°C for five hours. The final xerogel had a nominal composition of Cr(0.1)/Co(0.25)/Ti(0.5).

Example 7: Cr(0.2)/Au(0.025)/Al(0.775)

An aqueous $AuCl_3$ solution (28.822 mL, 0.3 M) was combined with an aqueous solution of $Cr_3(OH)_2(CH_3CO_2)_7$ (4.095 mL, 1.689 M in Cr) and an aqueous Al_2O_3 colloid (5.742 mL, 4.668 M (as Al)) in a 150 mL petri dish with gentle swirling. A NaOH solution (1.340 mL, 0.01 M) was added both for Na content and to destabilize the colloid and induce gellation by altering pH. A red brown gel formed, and the material was aged for at least two days prior to drying under vacuum at 120°C for five hours. The final xerogel had a nominal composition of Cr(0.2)/Au(0.025)/Al(0.775).

Example 8: Cr(0.025)/Au(0.025)/Mg(0.95)

A magnesium methoxide solution (47.353 mL, 0.3495 M) formed by combining magnesium methoxide with 50 volume % ethanol and $AuCl_3$ (21.776 mL of 0.02 M) in absolute ethanol were simultaneously added to a 150 mL petri dish with gentle swirling under a nitrogen atmosphere. In a subsequent addition, an aqueous solution containing $Cr_3(OH)_2(ac)_7$ (0.871 mL, 0.5M in Cr) was added. A gel formed, and the dark gel, after aging for at least three days, was dried at 120°C under vacuum for 5 hours. The final xerogel had a nominal composition of Cr(0.025)/Au(0.025)/Mg(0.95).

Example 9: 10% Cr/1% Li/27% La/α-Al_2O_3

An aqueous solution of $LiNO_3$ (1.762 g) in distilled water was added by the incipient wetness technique to an alpha-alumina support (19.723 g, calcined at 900°C overnight before use). The solids were dried at 110°C for two hours. An aqueous solution of $La(NO_3)_3 \bullet 6H_2O$ (22.134 g) in distilled water was added by the incipient wetness technique to the dried solids. The solids were again dried at 110°C for two hours. An aqueous solution of $Cr(NO_3)_3 \bullet 9H_2O$ (23.087 g) in distilled water was added by the incipient wetness technique to the dried solids. Finally, the material was dried at 110°C for two hours followed by calcination at 900°C overnight. The final catalyst had a nominal composition of 10% Cr/1% Li/27% La/α-Al_2O_3.

Example 10: 2% Cr/1% Li/27% La/α-Al_2O_3

An aqueous solution of $LiNO_3$ (1.762 g) in distilled water was added by the incipient wetness technique to an alpha-alumina support (22.123 g, calcined at 900°C overnight before use). The solids were dried at 110°C for two hours. An aqueous solution of $La(NO_3)_3{\bullet}6H_2O$ (22.134 g) in distilled water was added by the incipient wetness technique to the dried solids. The solids were again dried at 110°C for two hours. An aqueous solution of $Cr(NO_3)_3{\bullet}9H_2O$ (4.617 g) in distilled water was added by the incipient wetness technique to the dried solids. Finally, the material was dried at 110°C for two hours followed by calcination at 900°C overnight. The final catalyst had a nominal composition of 2% Cr/1% Li/27% La/α-Al_2O_3.

Example 11: Freeze-Dried Cr_2O_3

An aqueous solution of $Cr_3(OH)_2(CH_3CO_2)_7$ (100 mL, 2.5603 M) was added to a 150 mL petri dish and rapidly frozen with liquid nitrogen. The frozen solid was dried under vacuum for several days (approximately 7 days) to produce a freeze dried powder of pure Cr_2O_3. The freeze dried material was heated in air at 350°C for 5 hours and 525°C for 1 hour prior to use.

Example 12: Aerogel Cr_2O_3

Aerogel synthesis using a sol gel chemistry (Cr_2O_3 derived from the reaction of CrO_3 and methanol to produce a Cr_2O_3 gel, followed by supercritical extraction to produce a high surface area oxide (>500m^2/g). 16 g of chromium trioxide (CrO_3, Aldrich 23, 265-7) was dissolved in 24 ml of water, and added to 420 ml of methanol and 36 ml of additional water. Three of these combined solutions were loaded into a 1 liter autoclave, which was sealed and heated over a four hour time period to 300°C and 3400 psig. After holding at this temperature and pressure for 120 minutes, the pressure was vented to 1000 psig over 2 hours while maintaining 300°C. Pressure was finally vented to 1 atmosphere by bleeding at a rate of 10 psig per minute while maintaining 300°C, and the material was allowed to cool overnight. A Cr_2O_3 aerogel is formed by this procedure (reaction of $CrO_3 + CH_3OH \rightarrow Cr_2O_3$ + other oxidation products of ethanol (e.g., formaldehyde)). The surface area of materials formed by this procedure 537 m^2/g, as determined by N_2 BET analysis, and is X-ray (diffraction) amorphous.

Example 13: (Comparative Example) "Newport Chrome"

A commercially prepared catalyst manufactured by DuPont at the Holly Run site, by the pyrolysis of ammonium dichromate, $(NH_4)_2Cr_2O_7$, was tested for comparative purposes.

Example 14: $Co_{0.2}$ $Cr_{0.8}$ Ox

(E97659-33B). An identical procedure was followed to generate the catalyst. 12 ml of $Co(NO_3)_2.6H_2O$ 1.0826M was combined with 20.30 ml of 2.5603M (1/3 $(Cr_3(OH)_2(CH_3CO_2)_7$, Aldrich 31,810-8) to form an aqueous solution which was frozen and freeze-dried as described in Example 11.

Example 15: $Co_{0.8}$ $Cr_{0.2}$ Ox

(E976559-33D). An identical procedure was followed to generate the catalyst. 48 ml of $Co(NO_3)_2.6H_2O$ (Aldrich, 23,037-5), 1.0826M was combined with 5.07 ml of 2.5603M (1/3 $(Cr_3(OH)_2(CH_3CO_2)_7$, Aldrich, 31,810-8) to form an aqueous solution which was frozen and freeze-dried as described in Example 11.

Example 16: $Co_{0.5}$ $Cr_{0.5}$ Ox

An identical procedure was followed to generate the catalyst. 30 ml of $Co(NO_3)_2.6H_2O$ (Aldrich, 23,037-5), 1.0826M was combined with 12.69 ml of 2.5603M (1/3 $(Cr_3(OH)_2(CH_3CO_2)_7$, Aldrich, 31,810-8) to form an aqueous solution which was frozen and freeze-dried as described in Example 11.

Example 17: CoOx (Comparative Example)

(E97659-33A). 60 ml of a solution containing $Co(NO_3)_2.6H_2O$ (Aldrich, 23,037-5) 1.0826 M was rapidly frozen in liquid nitrogen, placed in a freeze dryer (Virtis Corporation, shelves refrigerated to O°C) and evacuated to dryness over a period of 5-7 days, or until completely dry. The material was calcined in air according to the following schedule: 5°C/min to 525°C, 525°C for 1 hour; 10°C/min to room temperature. The material was pelletized and sieved prior to the reactor evaluation.

Test Procedure

Catalysts were evaluated in a 25 cm long quartz tube reactor equipped with a co-axial, quartz thermocouple well, resulting in a 4 mm, reactor i.d. The void space within the reactor was packed with quartz chips. The catalyst bed was positioned with quartz wool at approximately mid-length in the reactor. A three point, K type, thermocouple was used with the catalyst's "hot spot", read-out temperature reported as the run temperature. The catalyst bed was heated with a 4 inch (10.2 cm), 600 W band furnace at 90% electrical output. Mass flow controllers and meters regulated the feed composition and flow rate. Prior to start-up, the flows were checked manually with a bubble meter and then the feed composition was reconfirmed by gas chromatographic. analysis. The flow rates of all the meters were safety interlocked and their measurements were checked electronically by the mass flow meters every second. All runs were performed at a CH_4:O_2 feed ratio of 2:1, safely outside of the flammable region. Specifically, the feed contained, in volume%, 30% CH_4, 15% O_2 and 55% N_2. Experiments were conducted at 5 psig (136 kPa). The reactor effluent was analyzed by a gas chromatograph (g.c.) equipped with a thermal conductivity detector. The feed components (CH_4, O_2, N_2) and potential products (CO, H_2, CO_2, and H_2O) were all well resolved and reliably quantified by two chromatography columns in series consisting of 5A molecular sieve and Haysep T. Mass balances of C, H, and O all closed at 98-102%. Runs were conducted over two operating days, each with 6 hours of steady state, run time. The results, shown in **Table 1**, are reported at steady state and showed no evidence of catalyst deactivation after 12 hours, according to g.c. analysis.

TABLE 1

Example No.	Catalyst Composition*	V(mL)	Wt.(g)	Temp. °C	GHSV x10^4	%CH_4/O_2 Conv.	%CO/H_2 Sel.	H_2:CO	%Coke
1	$Cr_{0.1}La_{0.9}$	2	2.1417	770	6.1	58/100	83/73	1.8	0.08
2	$Cr_{0.025}Mg_{0.975}$	2	0.9024	710	6.1	45/100	74/48	1.3	2.99
3	$Cr_{0.2}Mg_{0.4}Si_{0.4}$	2	1.3851	875	6.1	64/100	93/50	1.1	1.83
4	$Cr_{0.1}Ce_{0.9}$	0.4	0.5972	860	3.045	36/100	49/45	1.8	n.d.
5	$Cr_{0.1}Sm_{0.9}$	0.4	0.5350	870	3.045	48/100	65/66	2.0	0.17
6	$Co_{0.25}Cr_{0.25}Ti_{0.5}$	2	1.0605	980	6.1	82/100	93/92	2.0	n.d.
7	$Au_{0.25}Cr_{0.2}Al_{0.775}$	0.7	0.5685	911	17.4	28/92	60/25	0.8	9.98

8	$Au_{0.25}Cr_{0.025}Mg_{0.95}$	2	0.9560	915	6.1	48/100	84/44	1.0	22.19
9	10%Cr,1%Li/27%La/α-Al_2O_3	0.9	1.0235	850	6.1	90/100	97/90	1.9	n.d.
10	2%Cr,1%Li,27%La//α-Al_2O_3	0.4	0.5327	830	3.045	90/100	96/93	1.9	2.69
11	Cr_2O_3 (freeze dried)	2	2.3529	670	6.1	72/100	91/85	1.9	n.d.
12	Cr_2O_3 (Xerogel)	0.4	0.2180	550	3.045	21/99	0/0	n/a	n.d.
13	Cr_2O_3 (Newport)	0.4	0.0778	655	30.5	29/64	70/30	0.86	n.d.
14	$Co_{0.2}Cr_{0.8}$	2	2.1793	630	6.1	96/100	98/97	1.98	0.39
15	$Co_{0.8}Cr_{0.2}$	2	2.2806	670	6.1	93/100	96/96	2.00	n.d.
16	$Co_{0.5}Cr_{0.5}$	2	1.9917	650	6.1	95/100	98/97	1.98	n.d.

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n.d. = none detected

* mole %

The recovered (after use) Cr_2O_3 catalyst of Example 11 showed no weight loss after thermal gravimetric analysis in air at 600°C to 700°C; no significant carbon deposition (coking) is apparent using this analytical method.

With reference to **Fig. 1**, comparing catalyst performance of the catalysts from Examples 11, 12 and 13, it can be appreciated that the catalyst preparation procedure has a major impact on catalyst performance. The catalyst of Example 11 was prepared by freeze drying chromium oxide precursors (e.g., chromium hydroxide acetate), followed by calcination at 525°C, which appears to produce a catalyst precursor with superior (best) performance (i.e., highest conversion and selectivity). The catalyst of Example 12 was prepared by aerogel synthesis using a sol gel chemistry (Cr_2O_3 derived from the reaction of CrO_3 and methanol to produce a Cr_2O_3 gel, followed by supercritical extraction to produce a high surface area oxide (>500m^2/g). The catalyst of Example 13 is a commercially available catalyst, "Newport Chrome," manufactured by DuPont at the Holly Run site. It is commercially prepared by pyrolyzing ammonium dichromate, $(NH_4)_2Cr_2O_7$. Chromium oxide prepared by freeze drying an aqueous solution of chromium hydroxide acetate, followed by calcination in air at 525°C, is clearly the most active and selective catalyst, as shown in **Fig. 1** and in **Table 2**, although this result could not have been predicted from previous work with chromium catalysts. Other major differences in performance between the catalysts of Examples 11-13 are also noted in **Table 2**. The "coke" and carbon content of the catalysts were determined on samples which were evaluated, and indicated in the last column of the table. The first number is derived from TGA analysis, and is the percentage weight loss of the sample above 600°C in air. The second number is determined by an elemental analysis technique involving combustion of the catalyst and analysis of CO/CO_2 which is produced.

TABLE 2

Millisecond Contact Time Reactor Data,[a] Chromium Oxide

Catalyst	Vol (mL)	Wt. (g)	Temp. (°C)	GHSV x 10^4	$\%CH_4/O_2$ Conv.	$\%CO/H_2$ Sel.	H_2:CO Ratio	% Coke
Cr_2O_3 (freeze dried)	2.0	2.3529	670	6.1	72/100	91/85	1.90	n.d.[b]/0.32
Cr_2O_3 (Xerogel)	0.4	0.2180	550	3.0	21/99	0/0	n/a	n.d.[b]
Cr_2O_3 (Newport)	0.4	0.0778	655	30	29/64	70/30	0.86	0.05
$Co_{0.2}Cr_{0.8}$	2.0	2.1793	630	6.1	96/100	98/97	1.98	0.39/2.2
$Co_{0.5}Cr_{0.5}$	2.0	1.9917	650	6.1	95/100	98/97	1.98	n.d.[b]/5.2
$Co_{0.8}Cr_{0.2}$	2.0	2.2806	670	6.1	93/100	96/96	2.00	n.d.[b]/21.6

[a] Feed: 30% CH_4, 15% O_2, 55% N_2

[b] not detected

The conventional view is that chromium promoters or additives promote non-selective reaction pathways for alkane oxidation reactions using molecular oxygen, O_2. Therefore, the selective behavior of chromium oxide-based compositions as catalysts for the partial oxidation of methane to CO and H_2, as disclosed herein, is unexpected and even surprising. In one inventor's experience with n-butane oxidation, for example, it was observed that chromium promoters in vanadium phosphorus oxide catalysts increased catalyst activity at the expense of selectivity. In these cases the catalysts were compared at the same percent conversion of reactant. A similar trend was also noted by Oganowski, W. et al. ("Promotional Effect of Molybdenum, Chromium and Cobalt on a V-Mg-O catalyst in oxidative dehydrogenation of ethylbenzene to styrene," Applied Catalysis A: General 136 (1996) 143-159.) At page 156 of that reference, the reaction chemistry is the oxidative dehydrogenation of ethylbenzene to styrene: "The molybdenum, chromium or cobalt doped V-Mg-O catalyst changes its activity and selectivity in the oxidative dehydrogenation of ethylbenzene. The specific activity decreases in the direction Cr,Co>Cr>Co>Mo while the selectivity increases in the direction: Cr>>Co,Cr,Co>Mo." This suggests that Cr would not serve as a selective catalyst for a process involving C-H activation, such as CH_4 partial oxidation, and is contrary to the inventors' present findings.

Although the reasons for these performance differences are under investigation, the selectivity changes may be related to the surface areas of the catalyst generated. Catalysts possessing the highest surface areas (i.e., a chromium oxide aerogel) also possess the lowest light-off temperatures and exhibit no selectivity to CO/H_2. This suggests that an increase in the number of sites for CO adsorption results in slower desorption from the catalyst surface, allowing for oxidation of CO. In the millisecond contact time reaction regime, a lower surface area catalyst possessing a limited number of active sites may actually be preferred for selective oxidation pathways.

Another important observation for the freeze dried catalyst systems is the near-absence of carbon deposition on the catalyst surfaces. This is clearly indicated for the pure chromium oxide freeze dried catalyst in the transmission electron microscopy (TEM) studies. **Fig. 2A** shows the crystal structure of the chromium oxide catalyst as prepared in Example 11. The freeze dried chromium oxide is comprised of highly crystalline powder containing well-faceted chromium oxide crystallites. Powder X-ray diffraction confirms the well-crystallized nature of this material. No change in catalyst appearance is apparent after reactor evaluation during an eight hour period, indicating stability of the material on stream over short time intervals. **Fig. 2B** shows the crystal structure of a sample taken after 6 hours on stream, indicating that there was no apparent change in crystallite size or morphology with time on stream in a reactor. After 6 hours on stream there is little carbon build-up (coking). A carbon deposit is indicated by the arrow in **Fig. 2B**. The surprisingly low carbon deposition may also be related to the lower surface area of the catalyst and the highly faceted, defect-free nature of the catalyst surface. Low carbon deposition and stability on stream (i.e., lack of sintering of chromium oxide particles) are very favorable catalyst properties for syngas catalysts.

X-ray diffraction (XRD) analysis of the Co/Cr materials of the representative catalysts of Examples 14-16 revealed that the $Co_{0.2}$ $Cr_{0.8}$ catalyst comprised, in the catalyst as calcined (heated in air), a mixture of $CoCr_2O_4$ (cubic spinel phase) and Cr_2O_3 (eskolaite, hexagonal/rhombohedral phase). In the final catalyst, after an 8 hour evaluation as described in **Table 2**, XRD analysis revealed Cr_2O_3 and possibly Co metal or a chromium carbide phase. Low carbon formation is a very unusual, unexpected, and advantageous feature of many of the Cr catalyst systems disclosed herein.

Additional catalyst systems were investigated to study trends in C-H activation. In this case, a series of rare earth promoted catalysts were synthesized and tested. **Fig. 3** is a graph showing trends in light-off temperature and basicity/ionicity of representative "support" matrix compositions (i.e., $Cr_{0.025}Mg_{0.975}O_x$; $Cr_{0.1}La_{0.9}O_x$; $Cr_{0.1}Ce_{0.9}O_x$; and $Cr_{0.1}Sm_{0.9}O_x$ from Examples 1, 2, 4 and 5.). The predicted ionicity or basicity of the compositions increases from right to left along the x-axis of the graph. These systems were chosen for their thermal stability. In addition, rare earth oxide base catalysts have been reported for methane coupling-type reactions. The basicity of these rare earth oxide systems may facilitate C-H activation. Trends in light-off temperature, or ignition temperature, suggest that this may be the case. A lanthanum chromium oxide compound (comprised of $La_2Cr_2O_6$ + Cr_2O_3 in powder X-ray diffraction studies) possesses the lowest light-off or ignition temperature. A plot of the light-off temperature versus the expected basicity or ionicity of the rare earth component shows a correlation which suggests C-H activation may be related to this property.

Thermogravimetric analysis (TGA) studies also indicate low carbon deposition for the rare earth oxide based chromium catalysts, as shown in **Fig. 4** for $La_{0.1}Cr_{0.9}O_x$ (La_2O_3 + $La_2Cr_2O_6$ by X-ray diffraction), prepared similarly to the method described in Example 11. In **Fig. 4**, the arrow at about 300°C indicates a temperature region where the catalyst undergoes carbonate decomposition and appreciable weight loss occurs. Carbon deposition, as indicated by the weight loss at about rt-350°C in N_2 is 6.548% (0.6889 mg). The weight loss from about 350-600°C is 2.897% (0.3048 mg), and from about 600-700°C is 0.08311 % (0.008744 mg). TGA analysis of weight loss in air (>600°C) indicates << 1 wt % carbon deposition for these catalyst systems after eight hours on stream (i.e., <0.07 wt % upon oxidation in air from 600-700°C for $La_{0.1}Cr_{0.9}O_x$)

A series of cobalt-containing chromium oxides are particularly interesting for this reaction chemistry. Initial studies on a $Co_{0.25}Cr_{0.25}Ti_{0.5}O_x$ system prepared using sol gel methods indicated that this catalyst was a promising catalyst system. A "freeze-dried" variant of this catalyst system, without titanium oxide, and prepared similar to the procedure in Example 11, exhibits the highest activity and selectivity, as shown in **Fig. 5** and **Table 2**.

Fig. 5 is a graph showing the reaction chemistry for several representative ternary freeze dried chromium oxides containing chromium and cobalt, and for chromium oxide and cobalt oxide alone. The reaction conditions included 30 % methane feed, 15% O_2 feed, 55% N_2 atmosphere, 6 hours on stream. X-ray diffraction analysis indicated the presence of Cr_2O_3 matrix and varying proportions of cobalt in the catalyst compositions tested. The low conversion and selectivity demonstrated by cobalt oxide in **Fig. 5** shows the beneficial effect of including chromium in the catalyst composition. This figure also indicates an optimal composition range for the specified reaction conditions (i.e., feed composition and flow rate of about 6.1×10^4 GHSV).

As shown in the X-ray diffraction data of **Figs. 6** and **7**, the cobalt chromium oxide materials consist of the cubic spinel ($CoCr_2O_4$) dispersed in a Cr_2O_3 matrix (hexagonal/rhombohedral phase, eskolaite). Before reactor evaluation **(Fig. 6B)** x-ray diffraction indicates a representative cobalt chromium oxide composition contains $CoCr_2O_4$ cubic spinel and Cr_2O_3. Following reaction in situ (i.e., on stream) the catalyst precursor $Co_{0.2}Cr_{0.8}Ox$ is reduced to cobalt metal and chromium oxide, as shown in **Fig. 6A**. This is not surprising considering the higher temperatures used in this methane oxidation reaction. **Figs 7A-C** contain the X-ray diffraction data for "reactor evaluated" catalysts having the following compositions, respectively: $Co_{0.2}$ $Cr_{0.8}$, $Co_{0.5}$ $Cr_{0.8}$, and $Co_{0.8}$ $Cr_{0.2}$. These compositions were prepared as described in Examples 14-16. Each of these samples show Co metal and Cr_2O_3, or pure Co. Ongoing studies in the inventors' laboratories are aimed at clarifying whether formation of the cubic spinel precursor is a required synthetic route for highest activity and selectivity (i.e., evolution of cobalt metal on stream from $CoCr_2O_4$).

These materials are highly active and selective catalyst systems (>95 % CH_4 conversion, 97-98 % selectivity to CO and H_2). As mentioned above, the low light-off temperatures of these materials (< 650°C) and superior performance make these catalyst systems favorable candidates for further improvement and commercialization. As might be expected for catalysts containing cobalt metal, the chromium oxide-based catalysts containing cobalt show carbon deposition on the reduced cobalt metal which is formed *in situ*. The amount of carbon deposition directly correlates with the cobalt metal in the composition. Transmission electron microscopy (TEM) studies indicate that turbostratic carbon is deposited mostly at the cobalt centers, and not on the chromium oxide support or matrix. Continuing studies by the inventors are directed toward reducing carbon deposition.

It is believed that lower cobalt levels and the addition of basic rare earth, alkaline or alkaline earth components may help minimize these acid catalyzed reactions.

As illustrated above, by choosing catalyst compounds or catalyst precursor materials which provide higher melting point pure ceramic oxides instead of metals, longer-life catalysts are obtained. By appropriate choice of catalyst composition, as demonstrated herein, sintering phenomena, which typically result in loss of catalytic surface area and eventually activity during use, can be diminished at high temperatures, thereby extending catalyst life. Some compositions which form metal plus ceramic oxide *in situ*, such as certain Co/Cr and Ni/Cr oxide compositions, may not share this advantage, however.

Process of Producing Syngas

Any suitable reaction regime may be applied in order to contact the reactants with the catalyst in a short contact time or millisecond contact time reactor. 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. For example, a feed stream comprising a hydrocarbon feedstock and an oxygen-containing gas is contacted with one of the above-described chromium-based catalysts in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising carbon monoxide and hydrogen. 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 contacted with the catalyst as a gaseous phase mixture with an oxygen-containing gas, preferably pure oxygen. The oxygen-containing gas may also comprise steam and/or CO_2 in addition to oxygen. Alternatively, the hydrocarbon feedstock is contacted with the catalyst as a mixture with a gas comprising steam and/or CO_2. 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. The process of the present invention may be operated at temperatures of from about 600°C to about 1,100°C, preferably from about 700°C to about 1,000°C. The hydrocarbon feedstock and the oxygen-containing gas are preferably pre-heated before contact with the catalyst. 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 2,000 to about 10,000,000 NL/kg/h, preferably from about 5,000 to about 5,000,000 NL/kg/h. Preferably the catalyst is employed in a millisecond contact time reactor for syngas production. The effluent stream of product gases, including CO and H_2, emerges from the reactor. Although not wishing to be bound by any particular theory, the inventors believe that the primary reaction catalyzed by the preferred catalysts described herein is the partial oxidation reaction of Equation 2, described above in the background of the invention. Alternatively, or additionally, other chemical reactions may also occur, catalyzed by the same catalyst composition. For example, in the course of syngas generation, intermediates such as $CO_2 + H_2O$ may occur as a result of the oxidation of methane, followed by a reforming step to produce CO and H_2. Also, particularly in the presence of carbon dioxide-containing feedstock or CO_2 intermediate, the reaction

$$CH_4 + CO_2 \rightarrow 2\,CO + 2H_2 \qquad (3)$$

may also occur during the production of syngas. Accordingly, the term "catalytic partial oxidation" when used in the context of the present syngas production method, in addition to its usual meaning, can also refer to a net catalytic partial oxidation process, in which a light hydrocarbon, such as methane, and O_2 are supplied as reactants and the resulting product stream is predominantly the partial oxidation products CO and H_2, in a molar ratio of approximately 2:1, rather than the complete oxidation products CO_2 and H_2O.

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 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.

CLAIMS

What is claimed is:

1. A chromium-based composition for catalyzing the conversion of a C_1-C_5 hydrocarbon to form a product gas mixture containing CO and H_2, the composition comprising:

   about 0.1-100 mole % of chromium or chromium-containing compound per total moles of metal or metal ion in said composition;

   at least one other elemental metal or metal-containing compound, the metal of which is chosen from the group consisting of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Zn, Cd, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Ni, Ru and Rh; and

   optionally, an oxidatively and thermally stable porous support,

   said composition comprising a structure other than a perovskite structure.
2. The composition of claim 1 wherein said porous support comprises at least one oxide or oxyhydroxide of a metal chosen from the group consisting of magnesium, silicon, titanium, tantalum, zirconium and aluminum.
3. The composition of claim 1 wherein said chromium or chromium-containing compound comprises about 10-100 mole % of the total moles of metal or metal ion in said composition.
4. The composition of claim 1 wherein said composition initially comprises a catalyst precursor comprising a metal/metal oxide, and after reaction in a syngas reactor, finally comprises a reduced metal and a metal oxide.
5. The composition of claim 4 wherein said catalyst precursor comprises $CoCr_2O_4$ and said reduced metal is zero valent cobalt metal and said metal oxide is Cr_2O_3. 6. The composition of claim 5 wherein said composition finally comprises reduced metal and/or metal oxide and substantially no deposited carbon after reaction in a syngas reactor.
7. The composition of claim 1 wherein said composition comprises a matrix structure chosen from the group consisting of xerogels and aerogels.
8. The composition of claim 7 wherein said matrix structure comprises said at least one oxide or oxyhydroxide of a metal chosen from the group consisting of magnesium, silicon, titanium, tantalum, zirconium and aluminum.
9. The composition of claim 1 wherein said matrix structure comprises at least 30 wt % of the total weight of said composition.

10. The composition of claim 1 wherein said matrix structure comprises about 30-99.9 mole % of the total moles (of metal) of said composition.

11. The composition of claim 1 wherein said matrix structure comprises about 50-97.5 mole % of the total moles (of metal) of said composition.

12. The composition of claim 1 wherein said matrix structure comprises titanium oxide/oxyhydroxide.

13. The composition of claim 1 wherein said matrix structure comprises magnesium oxide/oxyhydroxide and silicon oxide/oxyhydroxide.

14. The composition of claim 1 wherein the metal or metal ion of said at least one other elemental metal or metal-containing compound is cobalt.

15. The composition of claim 1 wherein the metal or metal ion of said at least one other elemental metal or metal-containing compound is lanthanum.

16. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is magnesium and silicon oxide/oxyhydroxide.

17. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is cerium.

18. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is samarium.

19. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is gold and aluminum oxide/oxyhydroxide.

20. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is gold, and magnesium oxide/oxyhydroxide.

21. The composition of claim 1 wherein the metal or metal-containing compound of said at least one other elemental metal or metal-containing compound is lanthanum, lithium and α-Al_2O_3.

22. The composition of claim 1 further comprising a catalyst support.

23. The composition of claim 22 wherein said support is an oxidatively and thermally stable catalyst support.

24. The composition of claim 23 wherein said support is a porous three-dimensional monolith.

25. The composition of claim 24 wherein said support is a reticulated ceramic or ceramic foam.

26. A process for preparing a chromium-based composition for catalyzing the conversion of a C_1-C_5 hydrocarbon to form a product gas mixture comprising CO and H_2, the process comprising combining

about 0.1-100 mole % elemental chromium or chromium-containing compound per total moles of metal in said composition,

optionally, at least one other metal or metal oxide the metal component of which is chosen from the group consisting of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, Ag, Au, Zn, Cd, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Co, Ni, Ru and Rh, and

optionally, at least one matrix-forming material chosen from the group consisting of the alkoxides of magnesium, silicon, titanium, tantalum, zirconium and aluminum; and

forming said combination into a porous solid.

27. The process of claim 26 wherein said combining step includes combining a matrix-forming material comprising at least 30 wt % of the total weight of said composition with said chromium compound and said at least one other metal compound.

28. The process of claim 27 wherein said matrix-forming material comprises titanium or titanium oxide.

29. The process of claim 27 wherein said matrix-forming material comprises a combination of oxides or alkoxides of magnesium and silicon.

30. The process of claim 26 further comprising:

preparing an intermediate composition comprising said chromium or chromium-containing compound and said at least one other metal or metal-containing compound; and

applying said intermediate composition to a porous matrix material comprising at least 30 wt % of the total weight of said composition.

31. The process of claim 30 wherein said step of applying comprises applying said intermediate composition to a porous monolith support.

32. The process of claim 31 wherein said intermediate composition is in the form of a liquid and said step of applying said intermediate composition to said porous matrix material comprises impregnating said porous matrix with said liquid.

33. The process of claim 26 wherein said forming comprises drying said composition.

34. The process of claim 33 further comprising thermally treating said composition.

35. The process of claim 34 wherein said step of thermally treating comprises thermally treating said composition *in situ* under reaction conditions.

36. The process of claim 33 wherein said step of forming comprises freeze-drying said intermediate composition.

37. The process of claim 33 wherein said step of forming comprises spray drying said intermediate composition.

38. The process of claim 33 wherein said step of forming comprises spray roasting said intermediate composition.

39. The process of claim 26 wherein said step of forming comprises forming a powder.

40. The process of claim 39 wherein said step of forming further comprises forming a pellet.

41. The process of claim 26 wherein said step of forming comprises forming an extrudate.

42. The process of claim 26 wherein said step of forming comprises forming a gel chosen from the group consisting of xerogels and aerogels.

43. The process of claim 26 wherein said matrix-forming material comprises at least one metal alkoxide.

44. The process of claim 43 wherein each said at least one metal alkoxide is chosen from the group consisting of metal alkoxides containing 1 to 20 carbon atoms.

45. The process of claim 44 wherein each said at least one metal alkoxide is chosen from the group consisting of metal alkoxides containing 1 to 5 carbon atoms.

46. The process of claim 43 wherein each said at least one metal alkoxide is a C_1-C_4 alkoxide chosen from the group consisting of tantalum n-butoxide, titanium isopropoxide and zirconium isopropoxide.

47. The process of claim 46 further comprising dissolving at least one said metal alkoxide in a non-aqueous medium to form an metal alkoxide solution.

48. The process of claim 47 further comprising mixing said metal alkoxide solution with a protic solvent whereby said at least one alkoxide reacts with said protic solvent to form a gel.

49. The process of claim 48 further comprising dissolving said chromium or chromium-containing compound in said protic solvent to form a protic catalytic metal solution.

50. The process of claim 49 wherein said protic solvent is water.

51. The process of claim 43 further comprising dissolving or suspending said matrix material in said non-aqueous liquid medium to form a non-aqueous matrix solution or colloidal suspension.

52. The process of claim 43 further comprising dissolving said at least one other elemental metal or metal-containing compound and said at least one matrix-forming component in a non-aqueous medium.

53. The process of claim 48 wherein said mixing comprises combining said protic solvent and said alkoxide in a molar ratio of about 5:1 to 53.1.

54. The process of claim 53 wherein said mixing comprises combining said protic solvent and said alkoxide in a molar ratio of at least about 26.5:1.

55. The process of claim 48 wherein said mixing comprises the gradual addition of sufficient protic solution to induce hydrolysis and condensation of said at least one metal alkoxide.

56. The process of claim 55 wherein said mixing comprises combining said water and said alkoxide in a molar ratio of about 0.1:1 to 10:1 water:alkoxide.

57. The process of claim 56 wherein said alkoxide is chosen from the group consisting of alkoxides of zirconium and titanium, and said mixing comprises combining said water and said alkoxide in a molar ratio of about 4:1.

58. A process for converting a C_1-C_5 hydrocarbon to a product gas mixture containing CO and H_2, the process comprising

mixing a C_1-C_5 hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock;

contacting said reactant gas mixture feedstock with a catalytically effective amount of the catalyst composition of any of claims 1-25;

during said contacting, maintaining said composition and said reactant gas mixture at a temperature of about 600-1,100°C;

during said contacting, maintaining said composition and said reactant gas mixture at a pressure of about 100-12,500 kPa; and

passing said reactant gas mixture over said composition at a continuous flow rate of about 2,000 to about 10,000,000 NL/kg/h.

59. The process of claim 58 wherein said step of maintaining said catalyst and said reactant gas mixture at conversion promoting conditions of temperature and pressure during said contacting includes maintaining a temperature of about 700-1,000°C.

60. The process of claim 59 wherein said step of maintaining said catalyst and said reactant gas mixture at conversion promoting conditions of temperature and pressure during said contacting includes maintaining a pressure of about 130-10,000 kPa.

61. The process of claim 60 further comprising mixing a methane-containing gas feedstock and an oxygen-containing gas feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1.

62. The process of claim 61 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 1.3:1 to about 2.2:1.

63. The process of claim 62 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 1.5:1 to about 2.2:1.

64. The process of claim 63 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 2:1.

65. The process of claim 58 wherein said oxygen-containing gas further comprises steam, CO_2, or a combination thereof.

66. The process of claim 58 further comprising mixing a hydrocarbon feedstock and a gas comprising steam and/or CO_2 to provide said reactant gas mixture.

67. The process of claim 58 wherein said C_1-C_5 hydrocarbon comprises at least about 50 % methane by volume.

68. The process of claim 67 wherein said C_1-C_5 hydrocarbon comprises at least about 75 % methane by volume.

69. The process of claim 68 wherein said C_1-C_5 hydrocarbon comprises at least about 80 % methane by volume.

70. The process of claim 58 further comprising preheating said hydrocarbon feedstock and said oxygen-containing feedstock before contacting said catalyst.

71. The process of claim 58 wherein said step of passing said reactant gas mixture over said catalyst comprises passing said mixture at a space velocity of about 5,000 to about 5,000,000 NL/kg/h.

72. The process of claim 58 further comprising retaining said catalyst in a fixed bed reaction zone.

73. A process for converting a C_1-C_5 hydrocarbon to a product gas mixture containing CO and H_2, the process comprising

mixing a C_1-C_5 hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock;

contacting said reactant gas mixture feedstock with a catalytically effective amount of the $CoCr_2O_4$ cubic spinel precursor dispersed in a chromium oxide matrix;

during said contacting, maintaining said composition and said reactant gas mixture at a temperature of about 600-1,100°C;

during said contacting, maintaining said composition and said reactant gas mixture at a pressure of about 100-12,500 kPa;

passing said reactant gas mixture over said composition at a continuous flow rate of about 2,000 to about 10,000,000 NL/kg/h;

reducing said catalyst precursor to cobalt metal in a chromium oxide matrix;

achieving greater than 95 % CH_4 conversion of said hydrocarbon in said reactant gas mixture; and

achieving at least about 97-98 % selectivity to CO and H_2 as products of the process.

74. A process for converting a C_1-C_5 hydrocarbon comprising at least about 80 vol% methane to a product gas mixture comprising CO and H_2, the process comprising:

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

preheating said gaseous feedstocks;

contacting said reactant gas mixture feedstock with a catalytically effective amount of a chromium-based composition containing

10-100 mole % (as the metal) of chromium or chromium-containing compound per total moles of metal or metal ion in said composition,

0-90% cobalt or cobalt-containing compound, and

optionally, an oxidatively and thermally stable porous support supporting said chromium or chromium-containing compound and said cobalt or cobalt-containing compound, said composition comprising a structure other than a perovskite structure;

during said contacting, maintaining said composition and said reactant gas mixture at a temperature of about 600-1,100°C;

during said contacting, maintaining said composition and said reactant gas mixture at a pressure of about 100-12,500 kPa; and

passing said reactant gas mixture over said composition at a continuous flow rate of about 2,000 to 10,000,000 NL/kg/h.

75. The process of claim 58 wherein said composition is nominally 0.8 mole % in elemental chromium or chromium ion and 0.2 mole % in elemental cobalt or cobalt ion.

76. The process of claim 58 wherein said composition is nominally 0.2 mole % in elemental chromium or chromium ion and 0.8 mole % in elemental cobalt or cobalt ion.

77. The process of claim 58 wherein said composition is nominally 0.5 mole % in elemental chromium or chromium ion and 0.5 mole % in elemental cobalt or cobalt ion.

78. The process of claim 58 wherein said composition is nominally 2-10 mole % chromium or chromium ion, 1 mole % in lithium or lithium ion and 27 mole % lanthanum or lanthanum ion and comprises an α-AlO_3 support.

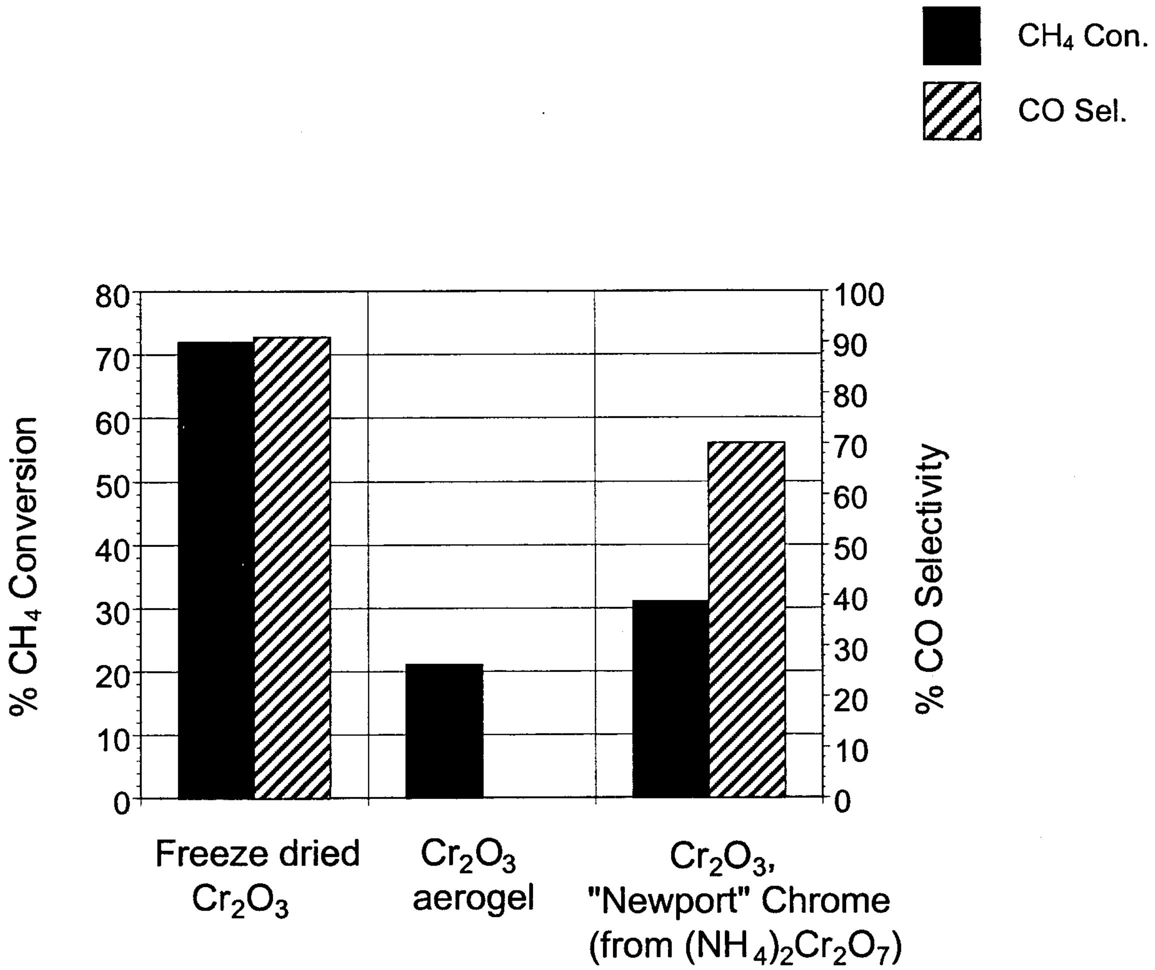
CH_4 Con.
CO Sel.
% CH_4 Conversion
% CO Selectivity
0
10
20
30
40
50
60
70
80
0
10
20
30
40
50
60
70
80
90
100
Freeze dried Cr_2O_3
Cr_2O_3 aerogel
Cr_2O_3, "Newport" Chrome (from $(NH_4)_2Cr_2O_7$)

FIG. 1

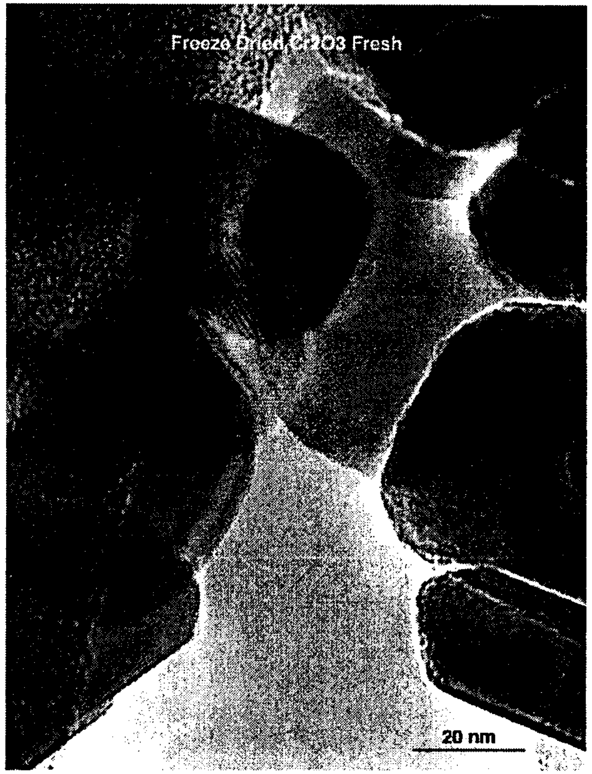
Freeze Dried Cr2O3 Fresh
20 nm

FIG. 2A

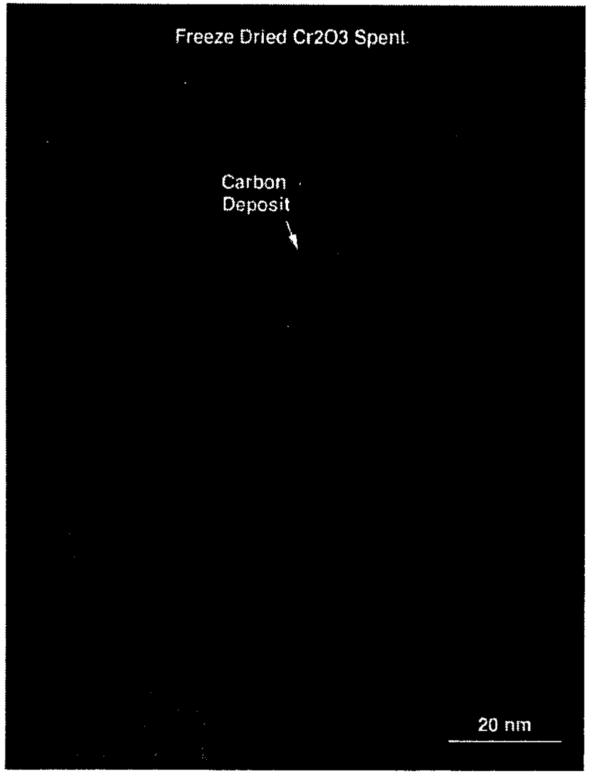
Freeze Dried Cr2O3 Spent.
Carbon Deposit
20 nm

FIG. 2B

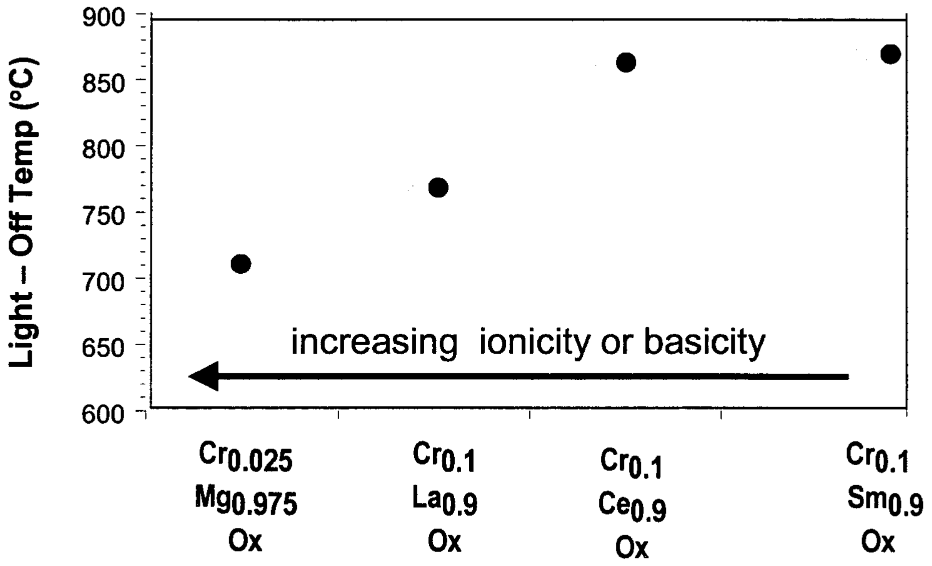
Light – Off Temp (°C)
900
850
800
750
700
650
600
increasing ionicity or basicity
Cr0.025 Mg0.975 Ox
Cr0.1 La0.9 Ox
Cr0.1 Ce0.9 Ox
Cr0.1 Sm0.9 Ox

FIG. 3

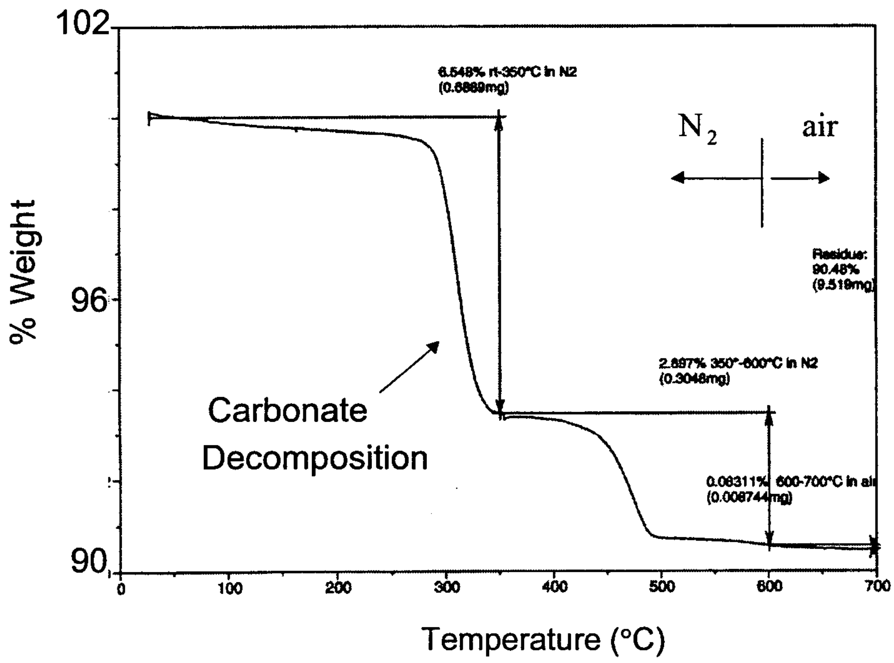
102
96
90
% Weight
0
100
200
300
400
500
600
700
Temperature (°C)
6.548% rt-350°C in N2
(0.6889mg)
N2
air
Residue:
90.48%
(9.519mg)
2.897% 350°-600°C in N2
(0.3048mg)
0.08311% 600-700°C in ai
(0.008744mg)
Carbonate
Decomposition

FIG. 4

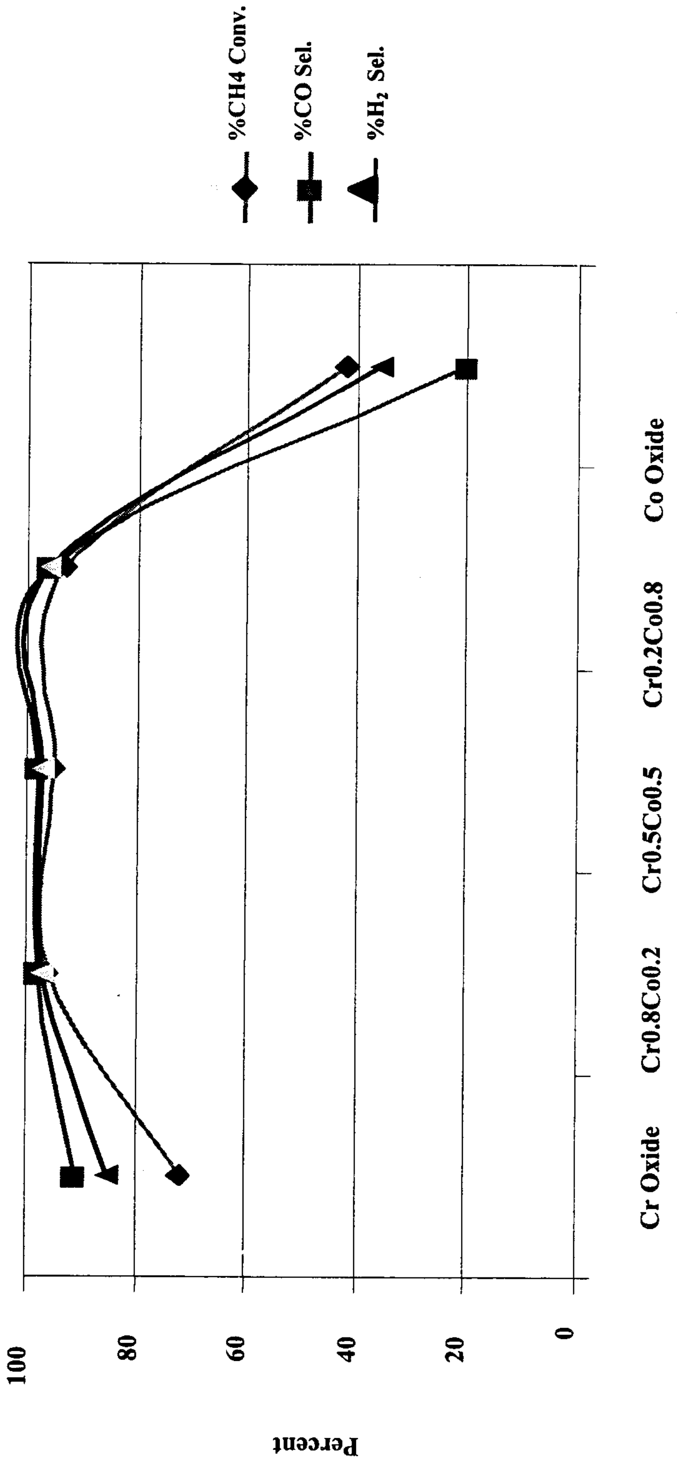
%CH4 Conv.
%CO Sel.
%H$_2$ Sel.
Percent
100
80
60
40
20
0
Cr Oxide
Cr0.8Co0.2
Cr0.5Co0.5
Cr0.2Co0.8
Co Oxide

FIG. 5

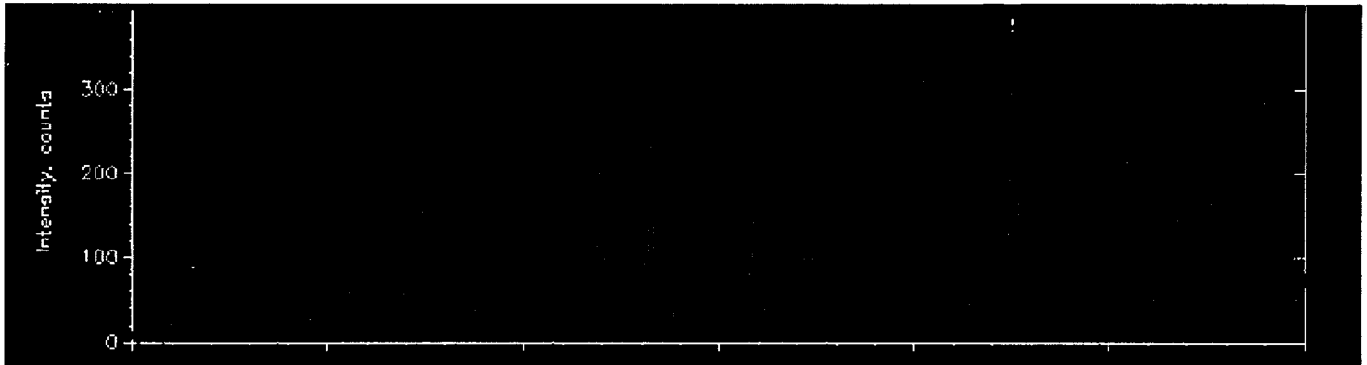
Intensity, counts
300
200
100
0

FIG. 6A

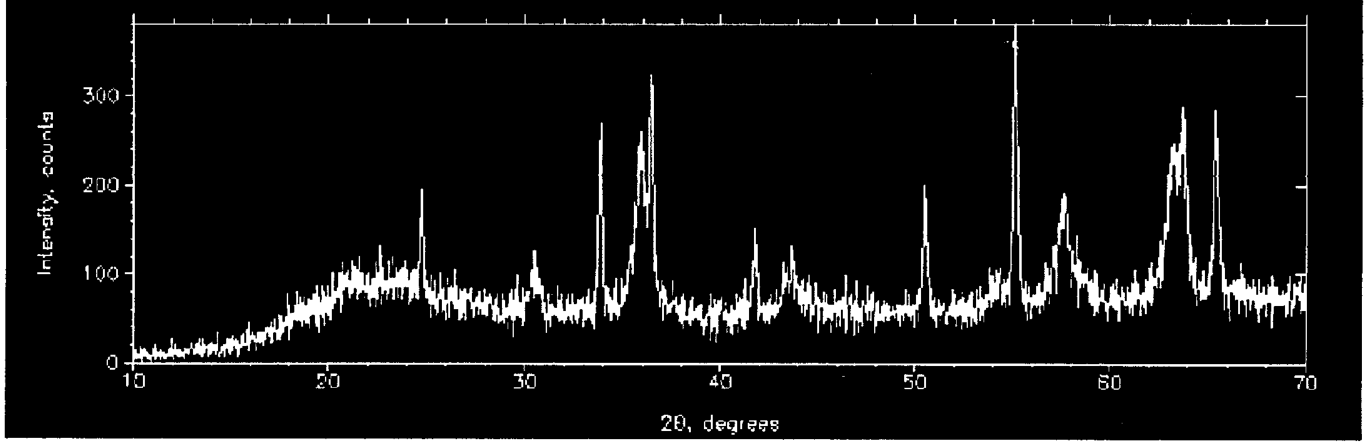
Intensity, counts
300
200
100
0
10
20
30
40
50
60
70
2θ, degrees

FIG. 6B

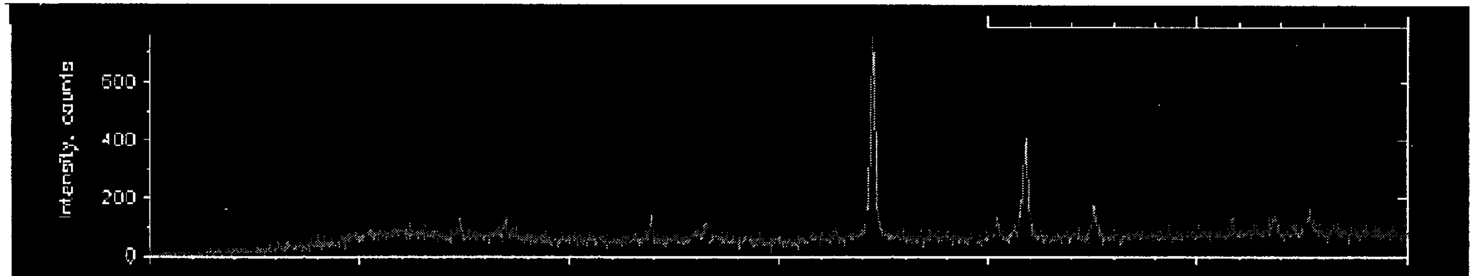

FIG. 7A

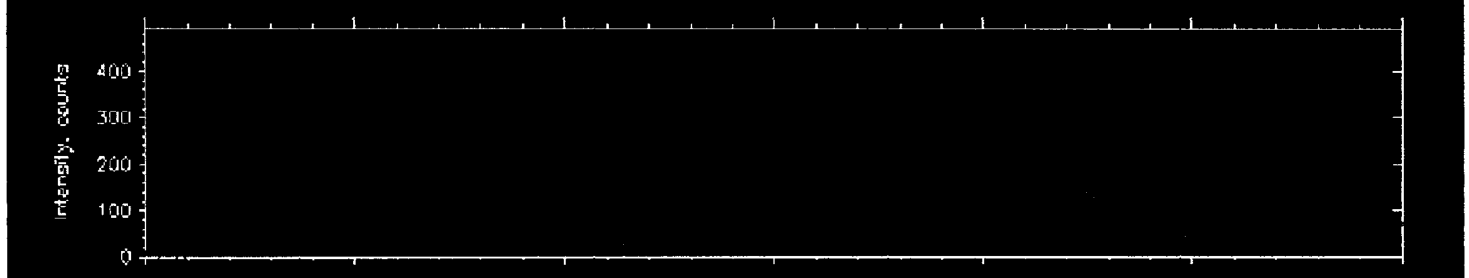

FIG. 7B

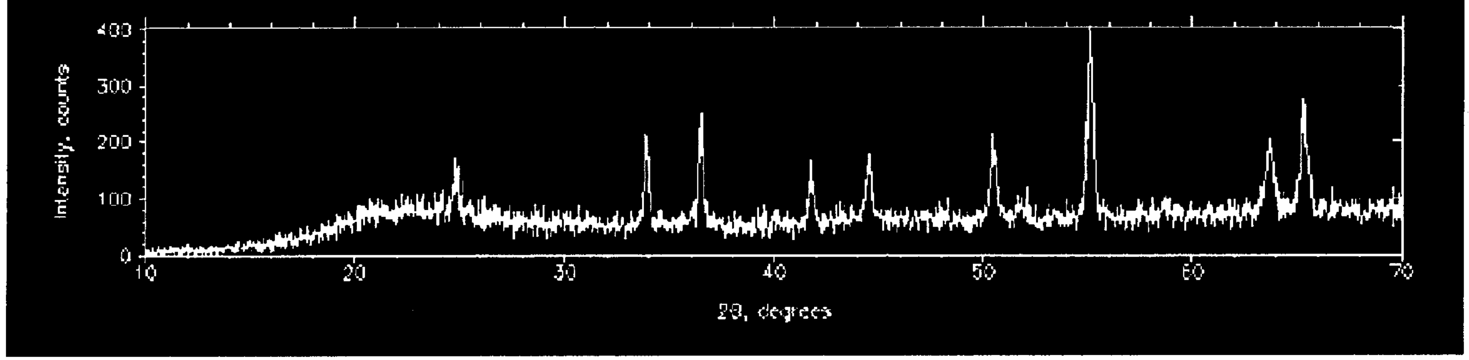

FIG. 7C

INTERNATIONAL SEARCH REPORT

Int :ional Application No
PCT/US 00/30287

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/40 C01B3/38 B01J23/26 B01J23/68

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 C01B B01J

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)

WPI Data, EPO-Internal, PAJ, INSPEC, COMPENDEX, API Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 262 947 A (JOHNSON MATTHEY PLC) 6 April 1988 (1988-04-06) examples ---	1-3,26, 58-78
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 9 February 2001	Date of mailing of the international search report 16/02/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Van der Poel, W

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INTERNATIONAL SEARCH REPORT

Int :ional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 656 317 A (SHELL INT RESEARCH) 7 June 1995 (1995-06-07) the whole document	58-78

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