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[54] HYDROCARBON SYNTHESIS FROM CO AND H_2 USING RU SUPPORTED ON GROUP VB METAL OXIDES

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[52] **U.S. Cl.** .... **260/449 R**; 252/432; 252/444; 252/435 R; 252/456; 252/458; 252/460; 252/464; 252/465; 252/466 PT

[58] **Field of Search** .... 260/449 R

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[57] **ABSTRACT**

An improved method for the synthesis of hydrocarbons with reduced methane formation and for the selective generation of olefinic hydrocarbons, preferably C_2-C_5 olefins inclusive, which method comprises the steps of passing a CO and H_2 synthesis gas stream over a catalyst at a temperature and pressure for a time sufficient to generate the desired olefinic products, wherein the improvement consists in using as a catalyst ruthenium on a support comprising at least one refractory Group VB metal oxide. The weight loading of the ruthenium may range from about 0.01 to about 15 wt. % based on the total catalyst weight. The ruthenium average crystallite size is preferably less than 5 nm (50Å). The operating conditions of the instant process are typical for Fischer-Tropsch synthesis.

17 Claims, No Drawings

HYDROCARBON SYNTHESIS FROM CO AND H_2 USING RU SUPPORTED ON GROUP VB METAL OXIDES

FIELD OF THE INVENTION

Brief Description of the Invention

An improved method for the synthesis of hydrocarbons with reduced methane formation and for the selective generation of olefinic hydrocarbons, preferably C_2–C_5 olefins inclusive, which method comprises the steps of passing a CO and H_2 synthesis gas stream over a catalyst at a temperature and pressure for a time sufficient to generate the desired olefinic products wherein the improvement consists in using as a catalyst ruthenium on a support comprising at least one refractory Group VB metal oxide. The weight loading of the ruthenium may range from about 0.01 to about 15 wt.% based on the weight of the total catalyst. The ruthenium average crystallite size is preferably less than 5 nm (50 Å). The operating conditions of the instant process are typical for Fischer-Tropsch synthesis.

DETAILED DESCRIPTION OF THE INVENTION

An improved method for the synthesis of hydrocarbons with reduced methane formation and for the selective generation of olefinic hydrocarbons, preferably C_2–C_5 olefins inclusive, which method comprises the steps of passing a CO and H_2 synthesis gas stream over a catalyst at a temperature and pressure for a time sufficient to generate the desired olefinic products wherein the improvement consists in using as a catalyst ruthenium on a support comprising at least one refractory Group VB metal oxide.

The instant invention presents an improvement in the Fischer-Tropsch hydrocarbon synthesis method in that it has been discovered unexpectedly that a ruthenium catalyst supported on a refractory Group VB metal oxide, or mixtures thereof, when utilized in conjunction with the Fischer-Tropsch method, will generate, with greater selectivity, olefinic hydrocarbons with reduced production of methane and other paraffinic products.

The instant process exhibits this selectivity to olefinic products, preferably C_2–C_5 olefins inclusive, when the catalyst utilized comprises ruthenium supported on a supported selected from the group consisting of a refractory Group VB metal oxide, or mixtures thereof, preferably V_2O_3, Nb_2O_5 and Ta_2O_5. The support may also be selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Ta_2O_5, SiO_2-Nb_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth-Group VB oxides, alkali-Group VB oxides, rare earth Group VB oxides, Group IVB-Group VB oxides, or mixtures thereof, but is preferably oxides of vanadium, oxides of tantalum and oxides of niobium or mixtures thereof or admixed with alumina, silica or Group IVB oxides. Most preferably, the support comprises essentially pure V_2O_3, Nb_2O_5 or Ta_2O_5 or mixtures thereof either alone or in combination with alumina, silica or Group IVB oxides. It is also possible to admix with these materials other refractory materials that will not substantially inhibit the Fischer-Tropsch hydrocarbon synthesis characteristics of ruthenium supported on at least one Group VB metal oxide as herein described. The supports which may be used in the practice of this invention may be in any form, such as powders, pellets, spheres, extrudates, etc. and may have a B.E.T. surface area of from about 1 to about 200 m^2g^{-1}, preferably from about 10 to about 100 m^2g^{-1}, most preferably from 25 to about 100 m^2g^{-1}. With most metal catalysts, the higher the surface area of the support, the higher the dispersion of the supported metal at a given weight loading. It is therefore desirable to use a support with as high a surface area as possible to maximize the dispersion of the ruthenium metal. Ruthenium is deposited on the chosen support in a concentration of from about 0.01 to about 15 wt.%, preferably from about 0.1 to about 10 wt.%, and most preferably from about 0.5 to about 5 wt.%, the percentages based on total weight of catalyst with the ruthenium possessing an average crystallite size, as determined by standard techniques such as X-ray diffraction of from about 1 to about 20 nm, preferably about 1 to about 10 nm, and most preferably from about 1 to about 5 nm. Using standard experimental techniques, for a ruthenium on Nb_2O_5(650), Ta_2O_5(650) or V_2O_3(650) system, reduced in hydrogen at 450° C., X-ray diffraction shows no particles of Ru in the reduced catalyst, indicating particles of Ru having crystallite sizes of less than 5 nm, which corresponds to a dispersion of greater than 20%.

Ruthenium catalysts comprising ruthenium supported on a support comprising a refractory Group VB metal oxide, or mixtures thereof, exhibit greater selectivity to the production of olefinic products with decreased methane formation as compared with typical ruthenium catalysts of the prior art. The prior art catalysts are either unsupported or supported on such materials as Al_2O_3, SiO_2 or carbon.

The operating conditions of the instant process are typical for Fischer-Tropsch synthesis. The pressure may range from about 100 to about 10^5 kPa, preferably from about 100 to about 3100 kPa, and most preferably from about 100 to about 2060 kPa. The temperature may range from about 100° to about 500° C., preferably from about 150° to about 400° C., and most preferably from about 150° to about 300° C. The H_2/CO ratio may range from about 0.1 to about 10, preferably from about 0.5 to about 4, most preferably from about 1 to about 3. The space velocity may range from about 100 hr^{-1} to about 50,000 hr^{-1}.

The ruthenium catalysts employed in the practice of the instant process are themselves prepared by techniques known in the art for the preparation of other catalyst systems, such as Ru on Al_2O_3, etc. A suitable ruthenium salt, such as ruthenium chloride, ruthenium nitrate or ruthenium acetate, etc., is dissolved in a solvent such as water or any other suitable solvent and stirred with the chosen Group VB metal oxide support system. After thorough mixing the mixture is allowed to dry and then heat treated in air at a temperature of from 100° to 150° C. or alternatively may be dried immediately by heating in air at a temperature of between 100° and 150° C. for several hours.

In a preferred embodiment, the ruthenium catalyst, prepared as outlined above, or by similar techniques, is heat treated in a reducing atmosphere such as hydrogen at a temperature greater than 300° C., preferably greater than 400° C., most preferably greater than 500° C., for from typically 0.5 to 4 hours, preferably from 1-2 hours. U.S. Ser. No. 771,396, filed Feb. 23, 1977, copending application of S. J. Tauster, L. L. Murrell and S. C. Fung, teaches the procedures of preparing catalysts by this method and is hereby incorporated by reference. It should be noted that this heat treating reduction step need not be practiced as a separate step, since the Fischer-Tropsch synthesis is practiced in a reducing atmosphere and will, therefore, have a similar reduction effect on the catalyst as the above step. The supported ruthenium catalyst system utilized in the instant process may have an average ruthenium crystallite size of preferably less than 5 nm.

The following examples are presented to illustrate and not limit the instant invention.

EXAMPLE 1

The selectivity in a Fischer-Tropsch synthesis for ruthenium catalysts supported by Nb_2O_5 is compared to ruthenium catalysts both unsupported and supported by support materials of the prior art.

A 1% Ru/Nb_2O_5 catalyst was prepared in the following manner. Nb_2O_5 was prepared by the addition of a methanolic solution of $NbCl_5$ to a methanolic solution of NH_4OH, producing a gel. The latter was washed with H_2O, then with 0.2 M NH_4NO_3, followed by another wash with H_2O. This gel was dried at 110° C. The dried gel was calcined in air at 600° C. for 16 hours. X-ray inspection of the calcined product indicated the presence of Nb_2O_5 with no other phases apparent. The surface area (B.E.T.) was 7.9 m^2/g. A portion of Nb_2O_5 was treated in flowing H_2 (20% in He) at 650° for 1½ hours. The product was labeled Nb_2O_5(650). X-ray inspection showed the presence of Nb_2O_5 and of NbO_2, the latter being in a lesser amount.

The Nb_2O_5 and Nb_2O_5(650) prepared in the above manner were impregnated by the method of incipient wetness with aqueous solutions of $RuCl_3$. The impregnates were dried at 110° C. The amount of $RuCl_3$ used was calculated to provide 1% Ru by total weight of catalyst after reduction in H_2. The $RuCl_3/Nb_2O_5$ was charged after drying into the catalytic reactor for in situ reduction in H_2.

The $RuCl_3/Nb_2O_5$(650) was treated in flowing H_2 (20% in He) at 650° C., for 1½ hours, then cooled in flowing He and passivated by treatment with flowing, dilute O_2 (1% in He) at 25° C. This material was thereupon charged into the catalytic reactor where it underwent in situ reduction in H_2.

The ruthenium metal catalyst was prepared as follows. NH_4OH was added to an aqueous solution of $RuCl_3$ precipitating $Ru(OH)_3$ which was subsequently dried at 110°-120° C. in air. It was then charged to the reactor and flushed with He at room temperature. The H_2 concentration in the He stream was slowly increased at a rate such that the sample did not heat up excessively. When 100% H_2 was flowing over the sample, the temperature was increased to 300° C. over a period of 1 hour and held at 300° C. for 1 hour. Subsequently it was cooled to reaction temperature in H_2 for catalytic studies. The ruthenium catalysts supported on carbon, SiO_2 and η-Al_2O_3 were made in a manner similar to the Ru/Nb_2O_5: the ruthenium was deposited on the supports by the incipient wetness technique using $RuCl_3$; they were dried at 110°-120° C. in air; and reduced in situ. The carbon for the ruthenium on carbon catalyst was Carbolac-1, obtained from the Cabot Corporation, had a B.E.T. surface area of 950 m^2g^{-1}. The SiO_2 for the ruthenium on SiO_2 catalyst was Cab-O-Sil (HS-5), obtained from the Cabot Corporation, had a B.E.T. surface area of 300 m^2g^{-1}. The Al_2O_3 for the ruthenium on η-Al_2O_3 was prepared by calcining alumina B-trihydrate ($Al_2O_3.3H_2O$), obtained from Davison Chemical Co., at 600° C. in air for 4 hours. It had a B.E.T. surface area of 245 m^2g^{-1}.

TABLE I

SELECTIVITY OF VARIOUS RUTHENIUM CATALYSTS
(Reaction Conditions: H_2/CO = 3; Pressure = 103 kPa)

			Hydrocarbon Product Distribution (Mole %)								
Catalyst	T°C.	% CO Conv	CH_4	C_2H_4	C_2H_6	C_3H_6 C_3H_8	C_4H_8 C_4H_{10}	C_5H_{10} C_5H_{12}	C_6^+	C_2-C_5 Olefins	C_2^+
Ru metal[c]	226	3.5	96	0	4	TR.	0	0	0	0	4
4% Ru/Carbon[b]	243	2.5	98	0	2	TR.	0	0	0	0	2
	234	1.6	98	0	2	0	0	0	0	0	2
1% Ru/SiO_2[a]	232	4.1	87	½	7	4	1	1	TR.	2½	13
5% Ru/SiO_2[a]	233	16.7	86	TR.	8	4	1½	1	TR.	TR.	14
1% Ru/Al_2O_3[a]	228	8.8	66	----12----		8½	6	4½	3	11	34
	244	14.1	71	----11----		7	5	4	2	10	29
Ru/Al_2O_3[a]	239	13.6	67	½	10	10	10	6	5	—	33
1% Ru/Nb_2O_5[a]	234	7.8	48	----11----		13	10	7	12	22	52
1% Ru/Nb_2O_5(650)[a]	244	5.7	41	----14----		18	11	11	5	27	59

[a]Catalysts reduced for 1 hour at 450° C. before feed introduced.
[b]Catalyst reduced for 1 hour at 400° C. before feed introduced.
[c]Catalyst reduced for 1 hour at 300° C. before feed introduced.

Table I illustrates in a Fischer-Tropsch synthesis the desirable selectivity characteristics of Ru/Nb_2O_5 catalysts as compared with unsupported Ru metal or with catalysts consisting of ruthenium supported on other support materials. In particular, it should be noted that the formation of methane is significantly lower for the Ru/Nb_2O_5 catalysts than for the other catalysts listed. Thus, whereas the selectivity in the production of C_2+ is up to 34 mole % for all the other catalysts listed in Table I, values up to 59 moles % are obtained for a Ru catalyst supported on Nb_2O_5. A further desirable feature of the Ru/Nb_2O_5 catalyst is its enhanced formation of C_2-C_5 olefins. These olefins are useful chemical intermediates for the production of plastics, rubber, alcohols, ketones, aldehydes, esters and acids. It is shown in Table I that the Ru/Nb_2O_5 catalysts exhibit at least twice the selectivity in the production of C_2-C_5 olefins as any other catalyst listed.

EXAMPLE 2

The selectivity in a Fischer-Tropsch synthesis for ruthenium catalysts supported by Ta_2O_5 is compared to ruthenium catalysts both unsupported and supported by support materials of the prior art.

A 1% Ru/Ta_2O_5 catalyst was prepared in the following manner. Ta_2O_5 was prepared by the addition of a methanolic solution of $TaCl_5$ to a methanolic solution of NH_4OH, producing a gel. The latter was washed with H_2O, then with 0.2 M NH_4NO_3, followed by another wash with H_2O. This gel was dried at 110° C. The dried gel was calcined in air at 600° C. for 4 hours. X-ray inspection of the calcined product indicated the presence of Ta_2O_5 with no other phases apparent. The material was recalcined in air at 700° C. for 16 hours. The surface area (B.E.T.) was 5.3 m^2/g.

A portion of the Ta_2O_5 was treated with flowing H_2 (20% in He) at 650° C. for 1½ hours. The product was labeled Ta_2O_5(650). X-ray inspection again showed Ta_2O_5 with no other phases apparent.

Ta_2O_5 and Ta_2O_5(650) were impregnated by the method of incipient wetness with aqueous solutions of $RuCl_3$. The amount of $RuCl_3$ was calculated to provide 1% Ru by weight after reduction in H_2. $RuCl_3/Ta_2O_5$ was charged, after drying, into the catalytic reactor for in situ reduction in H_2.

$RuCl_3/Ta_2O_5$(650) was treated in flowing H_2 (20% in He) at 650° C., for 1½ hours, then cooled in flowing He and passivated by treatment with flowing, dilute O_2 (1% in He) 25° C. This material was thereupon charged into the catalytic reactor wherein it underwent in situ activation in H_2. The other catalysts were prepared as described in Example 1.

Table II illustrates in a Fischer-Tropsch synthesis the desirable selectivity characteristics of Ru/Ta_2O_5 catalysts as compared with unsupported Ru metal or with catalysts consisting of ruthenium supported on other support materials. The other catalysts were prepared as described in Example 1. The data pertaining to Ru metal, Ru/carbon, Ru/SiO_2 and Ru/Al_2O_3 are identical to that presented in Table I and are repeated for convenience. It is seen that the desirable selectivity characteristics which were pointed out with respect to Ru/Nb_2O_5 catalysts in Table I also apply to Ru/Ta_2O_5 catalysts. Thus, the molar selectivities of the Ru/Ta_2O_5 catalyst in the production of C_2+ hydrocarbons are in excess of 50%—considerably greater than the molar selectivity to the C_2+ hydrocarbons of the prior art catalysts listed. Table II also indicates that the Ru/Ta_2O_5 catalysts exhibit markedly enhanced selectivity in the production of C_2–C_5 olefins as compared to any other catalyst listed.

TABLE II

SELECTIVITY OF VARIOUS RUTHENIUM CATALYSTS
(Reaction Conditions: H_2/CO = 3; Pressure = 103 kPa)

			Hydrocarbon Product Distribution (Mole %)								
Catalyst	T °C.	% CO Conv	CH_4	C_2H_4	C_2H_6	C_3H_6 C_3H_8	C_4H_8 C_4H_{10}	C_5H_{10} C_5H_{12}	C_6^+	C_2—C_5 Olefins	C_2^+
Ru metal[c]	226	3.5	96	0	4	TR.	0	0	0	0	4
4% Ru/Carbon[b]	243	2.5	98	0	2	TR.	0	0	0	0	2
	234	1.6	98	0	2	0	0	0	0	0	2
1% Ru/SiO_2[a]	232	4.1	87	½	7	4	1	1	TR.	2½	13
5% Ru/SiO_2[a]	233	16.7	86	TR.	8	4	1½	1	TR.	TR.	14
1% Ru/Al_2O_3[a]	228	8.8	66	----12----		8½	6	4½	3	11	34
	244	14.1	71	----11----		7	5	4	2	10	29
5% Ru/Al_2O_3[a]	239	13.6	67	½	10	10	10	6	5	—	33
1% Ru/Ta_2O_5[a]	228	17.7	46	----10----		13	10	11	9	17	54
1% Ru/Ta_2O_5(650)[a]	226	10.3	42	----10----		16	12	9	11	27	58

[a]Catalysts reduced for 1 hour at 450° C. before feed introduced.
[b]Catalyst reduced for 1 hour at 400° C. before feed introduced.
[c]Catalyst reduced for 1 hour at 300° C. before feed introduced.

EXAMPLE 3

The selectivity in a Fischer-Tropsch synthesis for ruthenium catalysts supported by V_2O_3 is compared to ruthenium catalysts both unsupported and supported by other support materials of the prior art.

A 1% Ru/V_2O_3 catalyst was prepared in the following manner:

V_2O_3 was made as follows: NH_4VO_3 was calcined at about 400° C. in flowing air to give V_2O_5. The surface area (B.E.T.) was 11 m^2/g. The V_2O_5 was reduced in flowing H_2 (20% in He) at 550° C. for 2½ hours. X-ray inspection showed V_2O_3 with a small extraneous signal at 2θ°=27°. The latter indicates the presence to a very small extent, of a crystallographic shear phase of the family, V_mO_{2m-1}. The surface area (B.E.T.) was 2.4 m^2/g.

A portion of V_2O_3 was treated in flowing H_2 (20% in He) at 650° C. for 1½ hours. The product was labelled V_2O_3(650). X-ray inspection indicated the presence of V_2O_3 with no other phases apparent. Thus, the very small amount of higher vanadium oxide present before H_2 treatment at 650° C. had been removed by this treatment.

V_2O_3 and V_2O_3(650) were impregnated by the method of incipient wetness with aqueous solutions of $RuCl_3$. The impregnates were dried at 110° C. The amount of $RuCl_3$ used was calculated to provide 1% Ru by weight after reduction in H_2. $RuCl_3/V_2O_3$ was charged, after drying, into the catalytic reactor for in situ reduction in H_2.

$RuCl_3/V_2O_3$(650) was treated in flowing H_2 (20% in He) at 650° C., 1½ hours, then cooled in flowing He and passivated by treatment with flowing, dilute O_2 (1% in He) at 25° C. This material was thereupon charged into the catalytic reactor where it underwent in situ activation in H_2.

Table III illustrates in a Fischer-Tropsch synthesis the desirable selectivity characteristics of Ru/V_2O_3 catalysts as compared with unsupported Ru metal or with catalysts consisting of ruthenium supported on other support materials. The data pertaining to Ru metal, Ru/Carbon, Ru/SiO_2 and Ru/Al_2O_3 are identical to that presented in Tables I and II and are repeated in Table III for convenience. It is seen that the desirable selectivity characteristics which were demonstrated with respect to Ru/Nb_2O_5 catalysts in Table I and Ru/Ta_2O_5 catalysts in Table II also apply to Ru/V_2O_3 catalysts. Thus, the molar selectivities of the Ru/V_2O_3 catalysts in the production of C_2+ are about 50%—considerably greater than the molar selectivity to the C_2+ hydrocarbons of the other catalysts listed. Formation of C_2–C_5 olefins is also markedly enhanced for Ru/V_2O_3. In the case of Ru/V_2O_3(650), formation of propylene, butene and pentene was not measured. However, the high selectivity with which ethylene is formed by this catalyst (17% or 16%, as compared with ½% over 5% Ru/Al_2O_3) is significant.

TABLE III

SELECTIVITY OF VARIOUS RUTHENIUM CATALYSTS
(Reaction Conditions: H_2/CO = 3, Pressure = 103 kPa)

			Hydrocarbon Product Distribution (Mole %)								
Catalyst	T °C.	% CO Conv	CH_4	C_2H_4	C_2H_6	C_3H_6 C_3H_8	C_4H_8 C_4H_{10}	C_5H_{10} C_5H_{12}	C_6^+	C_2-C_5 Olefins	C_2^+
Ru metal[c]	226	3.5	96	0	4	TR.	0	0	0	0	4
4% Ru/Carbon[b]	243	2.5	98	0	2	TR.	0	0	0	0	2
	234	1.6	98	0	2	0	0	0	0	0	2
1% Ru/SiO_2[a]	232	4.1	87	½	7	4	1	1	TR.	2½	13
5% Ru/SiO_2[a]	233	16.7	86	TR.	8	4	1½	1	TR.	TR.	14
1% Ru/Al_2O_3[a]	228	8.8	66	----12----		8½	6	4½	3	11	34
	244	14.1	71	----11----		7	5	4	2	10	29
5% Ru/Al_2O_3[a]	239	13.6	67	½	10	10	10	6	5	—	33
1% Ru/V_2O_3[a]	243	4.1	45	6	9	18	10	3	10	28	55
1% Ru/V_2O_3(650)[a]	246	0.7	55	17	4	17	6	—	—	—	45
	259	1.4	49	16	5	17	6	8	—	—	51

[a]Catalysts reduced for 1 hour at 450° C. before feed introduced
[b]Catalyst reduced for 1 hour at 400° C. before feed introduced
[c]Catalyst reduced for 1 hour at 300° C. before feed introduced

What is claimed is:

1. A process for the synthesis of olefins of from C_2 to C_5 chain length inclusive, said process comprising the steps of passing H_2 and CO at a H_2/CO ratio of 0.1 to about 10 over a catalyst comprising ruthenium on a support selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth-group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides and mixtures thereof, at a space velocity of from 100 to 50,000 hr^{-1}, at a temperature of from 100° to 500° C., at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic products wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15 wt. % based on total catalyst weight.

2. The process of claim 1 wherein the support comprising a Group VB metal oxide or mixture thereof is selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth-Group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides and mixtures thereof.

3. The process of claim 1 wherein the Group VB metal oxide is selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, and mixtures thereof.

4. The process of claim 1 wherein the Group VB metal oxide is V_2O_3.

5. The process of claim 1 wherein the group VB metal oxide is Nb_2O_5.

6. The process of claim 1 wherein the group VB metal oxide is Ta_2O_5.

7. The process of claim 1 wherein the ruthenium concentration is from about 0.1 to about 10 wt. % based on the total weight of the catalyst.

8. The process of claim 7 wherein the ruthenium concentration is from about 0.5 to about 5 wt. % based on the total weight of the catalyst.

9. The process of claim 2 wherein said ruthenium supported catalyst has a ruthenium particle crystallite size of from about 1 to about 20 nm.

10. The process of claim 9 wherein said ruthenium particle crystallite size is from about 1 to about 10 nm.

11. The process of claim 10 wherein said ruthenium particle crystallite size is from about 1 to about 5 nm.

12. The process of claim 1 wherein the catalyst is reduced at a temperature of greater than 300° C.

13. The process of claim 1 wherein the support has a surface area of from about 1 to about 200 m^2g^{-1}.

14. The process of claim 1 wherein the H_2/CO ratio is about 0.5 to about 4, the pressure is from about 100 to 3100 kPa and the temperature is about 150° to about 400° C.

15. The process of claim 1 wherein the H_2/CO ratio is about 1 to about 3, the pressure is from about 100 to about 2060 kPa and the temperature is about 150° to about 300° C.

16. The process of claim 14 wherein the support is Nb_2O_5.

17. The process of claim 14 wherein the support is Ta_2O_5.

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