PATENT SPECIFICATION (11) 1 583 571

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(21) Application No. 26596/77 (22) Filed 24 Jun. 1977
(44) Complete Specification Published 28 Jan. 1981
(51) INT. CL.^{3} C07C 1/02
(52) Index at Acceptance
C5E 221 222 332 386 391 CF
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(19)

(54) HYDROCARBON SYNTHESIS FROM CO AND H_2 WITH Ru, Ni, OR Rh SUPPORTED ON A TITANIUM OXIDE

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the synthesis of hydrocarbons from carbon monoxide and hydrogen.

According to the present invention, there is provided a process for the synthesis of hydrocarbons comprising passing H_2 and CO at H_2/CO ratio of 0.1 to 10 over a catalyst of ruthenium, nickel or rhodium supported on a titanium-containing oxide at a space velocity of up to 50,000 V/V/Hr. and 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 hydrocarbon products in the desired ratio.

In this patent specification, pressures are given in kilopascals (kPa) wherein a pascal is 1.450×10^{-4} pounds/in^2.

It was discovered by Pichler (see H. Pichler, Brenstoff-Chem. *19*, 226 (1938), H. Pichler and H. Buffleb, Brennstoff-Chem. *21*, 247, 273, 285 (1940)) in 1938 that Ru can produce at low temperatures and very high pressures, high molecular weight paraffinic waxes. Because it is such a good hydrogenation catalyst, ruthenium has not been noted for its capability to produce olefins. This is shown by the only study conducted under typical synthesis conditions using supported Ru where at 2160 kPa, 220-240°C. and H_2/CO ratios of 1 to 3, it was noted that the hydrocarbon product contained only "moderate" amounts of olefins (see F.S. Karn et al, I&EC Product Res. & Devel. *4*, 265 (1965)). At a H_2/CO ratio of 1, over 85 wt.% of the hydrocarbon product was composed of C_5+ material. In addition, at 100 kPa and 222°C., methane was the only hydrocarbon product observed. It is clear then that typical Ru catalysts would be expected to produce primarily high molecular weight paraffins at moderate pressures and methane as the principal product at atmospheric pressure.

Because it is so expensive, only supported, highly dispersed Ru catalysts can be considered for any commercial synthesis process since only in this state can the catalytic activity of most, if not all, of the Ru atoms to be utilized. It is necessary then to prepare these catalysts in such a way that they possess a large Ru surface area thereby reducing the weight loading of Ru required to achieve the desired activity. Since it is now possible to produce catalysts in this manner, they may now be seriously considered as candidates for the commercial synthesis of olefins and paraffins from CO and H_2.

A new method for the selective synthesis of olefinic hydrocarbons and particularly olefins of from C_2 to C_{10} chain length inclusive from CO and H_2 at pressures of from 100 to 10^5 kPa$_3$, preferably 100 to 3100 kPa, comprises the steps of passing a synthesis gas stream comprising CO and H_2 at a H_2/CO ratio of from 0.1-10, preferably 0.5-4, most preferably 1-3, at a space velocity of from 100 hr^{-1} over a catalyst comprising from 0.01 to 15 wt.% ruthenium on TiO_2, other titanium containing oxides or mixtures thereof for a time sufficient to effect the generation of desired olefinic hydrocarbon products at a temperature of from 100 to 500°C., preferably 1500-400°C., most preferably 150-300°C., and a pressure of from 100 to 10^5 kPa (1-1000 atm), preferably 100-3100 kPa, most preferably, 100-2060 kPa. The supported ruthenium catalyst system used in the instant process has a total BET surface area of from 10 to 60 m^2g-1 with a ruthenium crystallite size of preferably less than 5 mn (50Å).

Ruthenium supported on TiO_2, other titanium-containing oxides or mixtures of of titanium oxides, comprises a catalyst system which exhibits superior hydrocarbon synthesis characteristics in synthesis processes. The titanium containing oxide supports which may be used in the practice of this invention are oxides having surface areas of from 1 to 200 m^2g-1, preferably 10-100 m^2g-1, most preferably 25-100 m^2g-1. The oxides are selected from TiO_2, Al_2O_3-TiO_2, SiO_2-TiO_2, TiO_2-Carbon, $ZrTiO_4$, alkaline earth titanates ($BaTiO_3$, $CaTiO_3$, $SiTiO_3$, $MgTiO_3$) alkali titanates (Na_2TiO_3, Li_2TiO_3, K_2TiO_3) and rare earth titanates, preferably, the titanium oxide TiO_2. With most supported metal catalysts, the higher the surface area of the support, the higher the dispersion of the supported metal at a given metal loading. It is therefore desirable to use a TiO_2 with as high a surface area as possible to maximize the dispersion of the ruthenium metal. However, when working with TiO_2, samples with surface areas of 150 to 250 m^2g^{-1} (usually prepared by precipitation techniques) desurface on heating to ~ 500°C. Commercially available TiO_2 made by flame hydrolysis of $TiCl_4$ has a stable surface area of ~ 60 m^2g^{-1} for thermal treatments at temperatures of ~ 500°C. and is therefore the preferred support. For thermal treatments at temperatures below 500°C., TiO_2 prepared by precipitation techniques may be successfully employed. Ruthenium is deposited on the chosen support in a concentration of from 0.01 to 15 wt.%, preferably 0.1 to 10 wt.%, most preferably 0.5 to 5 wt.%, with the ruthenium possessing a crystallite size, as determined by standard techniques such as X-ray diffraction or transmission electron microscopy of from 1 to 20 nm, preferably 1-10 nm, most preferably 1-5 nm.

Using standard experimental techniques, for a ruthenium on TiO_2 system, reduced in hydrogen at 450°C., X-ray diffraction shows no particles of Ru in the reduced catalyst which indicates particles having crystallite sizes of less than 5 nm, which corresponds to a dispersion of greater than 20%.

Ruthenium catalysts supported on TiO_2, other titanium-containing oxides, or mixtures thereof, exhibit selectivity to olefin products, especially C_2-C_{10} inclusive olefins. Such catalysts, when used in the present system, exhibit improved selectivity to said olefins, improved longevity and tolerance to sulfur and resistance to ruthenium volatization in oxidizing atmospheres as compared with ruthenium catalysts of the prior art which are supported on materials such as Al_2O_3, SiO_2 or carbon.

The ruthenium catalysts employed in the practice of the present 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 nitriate or ruthenium acetate, etc., is dissolved in a solvent such as water or any suitable solvent and stirred with the chosen titanium oxide system. Preferably, the support is TiO_2 prepared by flame hydrolysis of $TiCl_4$, which TiO_2 has a surface area of ~60 m^2g^{-1}. 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.

However, there is a final step, which is essential, of heat treating the supported ruthenium catalyst, prepared as outlined above, or by similar techniques, 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 .5 to 4 hours, preferably 1-2 hours.

Nickel supported on TiO_2, other titanium-containing oxides or mixtures of various titanium oxides as described above comprises a catalyst system which exhibits superior hydrocarbon synthesis characteristics. Such supported nickel catalysts exhibit selectivity to paraffinic hydrocarbon products of from C_2 to C_7 which are free of olefins and oxygenated products. They generate CO conversions of up to 60% at pressures of 3090 kPa without significant change in product distribution. A large fraction of the product obtained contains 2 or more carbon atoms in the chain up to conversions of 60%. The supported nickel catalysts exhibit enhanced activity, improved selectivity to higher molecular weight normal paraffins, improved longevity and tolerance to sulfur and resistance to nickel carbonyl formation as compared to nickel catalysts on other supports such as Al_2O_3, silica or carbon.

Conventional nickel catalysts, i.e. Ni/Al_2O_3, Ni/SiO_2 etc. are well known for their selectivity toward methane formation; for example see M. Greyson, "Catalysis", Vol. IV, 473 (1956) and H. A. Dirksen and H. R. Linden, Research Bulletin #31, Institute of Gas Technology (1963). Within a wide range of temperature, pressure and H_2/CO ratios, methane is by far the predominant hydrocarbon product and it is this fact that has made nickel the catalyst of choice for commercial methane synthesis from CO and H_2.

Nicel has been dispersed on and co-precipitated with a wide variety of typical oxide supports and no major effect on product distribution has been noted. When higher hydrocarbons have been observed, they are still usually gaseous materials consisting primarily of ethane and only small quantities of C_3^+ hydrocarbons. The effect of a large number of promoters on the activity and selectivity of nickel catalysts has been studied and ThO_2 is the only material to have a pronounced influence on the product distribution. Usually used with

Ni/Kieselguhr catalysts, the addition of 12-24 parts ThO_2 per 100 parts Ni results in up to 60-70 wt.% of the total hydrocarbon product present as C_5^+ material including solids and liquids (see R.B. Anderson, "Catalysis", Vol. IV, p. 53 (1956)). No other promoters have been documented as being capable of inducing this change in product selectivity. Although catalyst activity was increased somewhat by the addition of ThO_2, the increases were not large, normally consisting of increases up to 10% in the H_2 + CO conversion.

Therefore, nickel catalysts have been used frequently in the past to synthesize methane from CO and H_2, and are quite selective in producing this product. With the exception of catalysts promoted with ThO_2, they were not known to possess the capability of producing large quantities of higher molecular weight prodcts. This invention discloses the modification of the catalytic behavior of nickel by dispersing it upon TiO_2 or a Ti-containing support resulting in a catalyst which is employed in a process which yields a much higher average molecular weight product. The highly desirable effect of greatly increasing the activity of the nickel component is also obtained.

A new method for the selective synthesis of higher molecular weight normal paraffins from CO and H_2 over a wide range of CO conversions at pressures of from 103 to 3090 kPa comprises the steps of passing a synthesis gas stream comprising CO and H_2 at a H_2/CO ratio of from 0.1-10, preferably 0.5-4, most preferably 1-3 at a space velocity of from 100 hr.$^{-1}$ to 50,000 hr.$^{-1}$ over a catalyst comprising from 0.01 to 75 wt.% Ni on TiO_2, other titanium-containing oxides or mixtures of said titanium-containing oxides for a time sufficient to effect the generation of desired paraffinic products at a temperature of from 100 to 500°C., preferably 150-400°C., most preferably 150-300°C. and a pressure of from 103-1.03 x 10^5 kPa, preferably 103-3090 kPa, most preferably 103-2060 kPa. The supported nickel catalysts system has a total BET surface area of from 10 to 60 m^{2}g^{-1} of total catalyst with a nickel crystallite size of preferably less than 10 nm (100Å) (as measured by X-ray diffraction). A suitable size range is 1-30 nm, preferably 1-10 nm, most preferably 1-7.5 nm.

Using standard experimental techniques, 10% Ni/TiO_2 reduced in hydrogen at 450°C. (as in the following examples) evaulated by X-ray diffraction exhibited a crystallite size of 7.5 nm which corresponds to a nickel dispersion of about 14%. For a 1.5% Ni/TiO_2 system, the particle size is less than 5 nm since Ni metal was not detectable by X-ray. This corresponds to a dispersion of greater than 20%.

The nickel catalysts employed in the practice of the present process are themselves prepared by techniques similar to those described above for ruthenium.

A supported Ni/TiO_2 catalyst can also be prepared by reduction of the compound $NiTiO_3$ which on reduction in hydrogen at temperatures of about 450°C. decomposes into nickel metal supported on TiO_2. Reduction of the stoichiometric $NiTiO_3$ to Ni/TiO_2 gives a catalyst of composition 38 wt.% Ni/TiO_2.

The final step of heat treating is as described above for the supported ruthenium catalyst.

The present process will selectively generate C_2^+ normal paraffins from CO and H_2 in conjunction with the above-described nickel catalyst systems provided operation is conducted at a temperature below 500°C. Use of the catalyst also allows synthesis to be run at temperatures lower than those disclosed in the prior art with equivalent product yields and CO conversion rates and such superior results are obtained when using catalysts possessing Ni weight loadings equal to those of the prior art.

Rhodium catalysts for the production of higher molecular weight hydrocarbons from CO and H_2 have been reported only in a Bureau of Mines Study (J.F. Shultz et al., U.S. Bureau of Mines Report #6974, 1967). This study showed that rhodium supported on Al_2O_3 produced 95 + wt.% methane at typical H_2/CO ratios, 2163 kPa pressure and at temperatures from 440-580°C. Because of its expense and low activity compared to other metals, rhodium was reported by these workers to be unattractive as a methanation catalyst.

It has now been found, however, that rhodium dispersed on TiO_2 or other titanium-containing oxide supports as described above has high activity and altered selectivity. Compared to Al_2O_3-supported rhodium, the use of TiO_2 or titanium-containing oxide-supported metal in olefin preparation processes results in a process which exhibits a marked decrease in methane in the products with a concomitant increase in the formation of higher molecular weight paraffins and olefins.

A new method for the improved synthesis of olefinic hydrocarbons and particularly olefins of from C_2 to C_5 chain length inclusive, and most particularly, C_3 and C_4 hydrocarbons from CO and H_2, comprises the steps of passing a synthesis gas stream comprising CO and H_2 at a H_2/CO ratio of from 0.1-10, preferably 0.5-4, most preferably 1-3 at a space velocity of from 100 hr^{-1} to 50,000 hr^{-1} over a catalyst comprising from 0.01 to 10 wt.% rhodium on TiO_2, other titanium-containing oxides or mixtures thereof for a time sufficient to effect the generation of desired olefinic hydrocarbon products in the desired ratio, said contacting being effected at a temperature of from 100 to 500°C., preferably 150-400°C., most preferably 150-300°C. and a pressure of from 100 to 10^5 kPa, preferably 100 to 3000 kPa, most preferably 100-2000 kPa. The supported rhodium catalyst system used in the instant process has a total BET surface area of from 10 to 60 m^2g^{-1} with a rhodium crystallite size of preferably less than 5 nm.

Rhodium is deposited on the chosen support in a concentration of from 0.01 to 10 wt.%, preferably 0.05-5 wt.%, most preferably 0.1-2 wt.%, with the rhodium possessing a crystallite size, as determined by standard techniques such as X-ray diffraction or transmission electron microscopy of from 1 to 20 nm, preferably 1-10 nm, most preferably 1-5 nm.

Using standard experimental techniques, for a rhodium on TiO_2 system reduced in hydrogen at 450°C., X-ray diffraction shows no particles of rhodium in the reduced catalyst which indicates that the rhodium crystallites possess an average size of less than 5 nm, which corresponds to a dispersion of greater than 20%.

The rhodium catalysts employed in the practice of the instant process are themselves prepared by techniques similar to those described above for ruthenium.

The final step of heat treating is as described above for the supported ruthenium catalyst.

Use of the above-identified catalyst in the present process at reaction conditions equivalent to those of the prior art gives superior results (in the way of improved selectivity and greater product yields) when catalysts possessing rhodium with loadings equal to those of the prior art are used.

EXAMPLE 1

Ruthenium catalysts with improved selectivity to olefin products and to hydrocarbons with carbon chain lengths of two carbons to ten carbons are obtained by depositing ruthenium on TiO_2 or titanium-containing oxide supports. Thus, a 2% Ru/TiO_2 catalyst is prepared by stirring together 10 grams of TiO_2 and 3 ml of $RuCl_3$ solution containing 0.2 g of ruthenium. The TiO_2 is prepared by the flame hydrolysis of $TiCl_4$ to give a support with 60 m^2g^{-1} surface area. Titania made by other techniques such as precipitation and calcination of a suitable salt is also satisfactory. After thoroughly mixing the TiO_2 and the ruthenium solution, the mixture is dried overnight in air at 110-120°C.

To illustrate the desirable properties of Ru/TiO_2 catalysts, they were compared to ruthenium supported on conventional supports such as Al_2O_3 or carbon. Thus, a 5% Ru/η-Al_2O_3 catalyst was prepared by thoroughly mixing 5.26 ml of $RuCl_3$ solution containing 0.526 grams of ruthenium with 10 grams of η-Al_2O_3. The resulting mixture was dried overnight in air at 110-120°C. A 4% Ru/carbon catalyst was prepared by thoroughly mixing 6 ml of $RuCl_3$ solution containing 0.12 grams of ruthenium with 3 grams of carbon with a surface area of $\sim 1000\ m^2g^{-1}$. The resultant mixture was dried overnight in air at 110-120°C.

The desirable selectivity characteristics of TiO_2 or titanium-containing oxide-supported ruthenium catalysts compared to other supports are demonstrated in Tables I, II and III. At 103 kPa total pressure Ru/TiO_2 shows a markedly different product distribution from Ru/Al_2O_3. The formation of methane and very high molecular weight hydrocarbons is suppressed over the Ru/TiO_2 catalysts giving a product spectrum in which the carbon chain length range of two to give carbon atoms is maximized. For Ru/Al_2O_3, much more methane and higher molecular weight hydrocarbons are produced. Ru/TiO_2 also possesses the desirable characteristics that a large fraction of the C_2-C_5 products is olefinic. Thus, this catalyst is particularly suitable for producing from CO and H_2 a product stream which is highly olefinic and with carbon chain lengths of two to five carbon atoms. Olefins such as ethylene, propylene, butenes and pentenes in this range are particularly desirable as chemical intermediates for the production of plastics, rubber, alcohols, ketones and aldehydes, esters and acids.

Table II illustrates the desirable selectivity characteristics of TiO_2 of titanium-containing oxide-supported ruthenium catalysts at higher total pressures of reactants. At 10^3 kPa the Ru/TiO_2 makes less methane and C_8 + hydrocarbons than Ru/Al_2O_3 with most of the products from Ru/TiO_2 being in the C_2 to C_7 carbon number range. Ru/TiO_2 thus exhibits improved selectivity to the desirable C_2 to C_7 hydrocarbons. Table II also illustrates the improved selectivity to olefins of Ru/TiO_2 compared to Ru/Al_2O_3. In the C_2 to C_5 carbon number range 42% of the products are olefins with Ru/TiO_2 whereas only 25% are olefins with Ru/Al_2O_3. Ru/TiO_2 is thus more selective for the production of the desirable olefins with carbon chain lengths of two to five carbon atoms.

Table III compares Ru/TiO_2 with ruthenium on a variety of other supports. Ruthenium supported on TiO_2 or titanium-containing oxide supports produces 42 wt.% of the products with carbon chain lengths of two to five carbon atoms, while ruthenium on Al_2O_3, carbon or ruthenium metal produce only 31%, 2% and 25%, respectively of products in this carbon number range. In addition, the fraction of olefins in the products is greatest for Ru/TiO_2 as indicated by the ethylene/ethane ratios for each catalyst. Ruthenium on Al_2O_3 or carbon, or unsupported ruthenium metal produce little or no ethylene in the C_2 fraction from CO and H_2 under the reaction conditions used in Table III whereas Ru/TiO_2 produces about one-half of the C_2 fraction as ethylene.

TABLE I

Selectivity of Ruthenium Catalysts

(Reaction Conditions: $H_2/CO = 1$, Pressure = 103 kPa)

Catalyst (a)	*Temp. (°C)*	*% CO Conv.*	*Product Carbon Number*	*Total wt %*	*wt % Olefin*	*wt % Paraffin*
2% Ru/TiO_2	262	0.7	C_1	26	—	—
			C_2	17	12	5
			C_3	28	20	8
			C_4	19	15	4
			C_5	10	7	3
			C_6^+	—	—	—
5% Ru/Al_2O_3	267	1.7	C_1	47	—	—
			C_2	13	5	8
			C_3	21	—	—
			C_4	7	6	1
			C_5	6	—	—
			C_6^+	5	—	—

(1 atm = 103 kPa)

(a) Each catalyst reduced 1 hour at 450°C prior to introducing feed at the realion temperature.

TABLE II

Selectivity of Ruthenium Catalysts
(Reaction Conditions; $H_2/CO = 1$, Pressure = 980 kPa)

Catalyst[a]	*Temp (°C)*	*% CO Conv.*	*Product Carbon Number*	*Total wt%*	*Wt% Olefin*	*wt% Paraffin*
2% Ru/TiO_2	267	7	C_1	14	-	-
			C_2	6	2	4
			C_3	21	14	7
			C_4	20	16	4
			C_5	17	10	7
			C_6	13	8	5
			C_7	9	5	4
			C_8^+	-	-	-
5% Ru/η-Al_2O_3	274	10	C_1	24	-	-
			C_2	6	1	5
			C_3	16	12	4
			C_4	11	6	5
			C_5	12	6	6
			C_6	11	-	-
			C_7	9	-	-
			C_8^+	12	-	-

(1 atm = 103 kPa)

(a) Each catalyst reduced 1 hour at 450°C prior to introducing feed at the reaction temperature.

TABLE III

Selectivity of Ruthenium Catalysts

(Reaction Conditions: $H_2/CO = 3$, Pressure = 103 kPa)

Catalyst	*T °C*	*% CO Conv.*	*Product Mole %*						
			CH_4	C_2H_4	C_2H_5	C_3H_6 C_3H_8	C_4H_8 C_4H_{10}	C_5H_{10} C_5H_{12}	C_6^+
2% $RuTiO_2$ (a)	228	1.8	54	6	5	16	10	5	4
5% Ru/Al_2O_3 (a)	229	10.6	66	1	9	6	9	6	4
4% Ru/Carbon (b)	234	1.6	98	0	2	0	0	0	0
Ru Metal Powder (c)	217	27.1	74	0	13	8	3	1	1

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

EXAMPLE 2

Catalysts with improved activity and selectivity to normal paraffin products with carbon chain lengths of two and higher are obtained by depositing nickel on TiO_2 and other titanium-containing oxide supports. Thus, a 1.5% Ni/TiO_2 catalyst is prepared by stirring 11.4 ml of nickel nitrate solution containing 0.39 g of nickel with 25 g of TiO_2 in a beaker. The TiO_2 was prepared by flame hydrolysis of $TiCl_4$ and had a surface area of 60 m^2g^{-1}. Titania made by other techniques such as precipitation and calcination of a suitable titanium salt is also satisfactory. After thoroughly mixing the nickel solution with the TiO_2 the resulting material is dried in a dessicator overnight and further dried in air in an oven at 120°C. overnight. Alternatively the resulting material can be dried immediately at 120°C. in air for several hours. A 10% Ni/TiO_2 catalyst is prepared by mixing with a spatula in a beaker 20 g of TiO_2 with 11.1 g $NiNO_3.6H_2O$ dissolved in 5 ml of distilled water. The resultant material is dried in a dessicator overnight and further dried at 120°C. in air overnight. By impregnating the dried 10% Ni/TiO_2 catalysts with additional quantities of nickel nitrate solution concentrations of Ni/TiO_2 up to ~75 wt.% can be obtained.

To illustrate the desirable characteristics of the Ni/TiO_2 catalysts, they were compared to several commercial nickel catalysts and to several nickel catalysts supported on Al_2O_3 and SiO_2. Thus a 5% Ni/η-Al_2O_3 catalyst was prepared by thoroughly mixing 9.5 g of η-Al_2O_3 having a surface area of 245 m^2g^{-1} with 6.6 ml of nickel nitrate solution containing 0.5 g nickel. The resulting mixture was dried overnight in air at 110°C. A 16.7% Ni/SiO_2 catalyst was prepared by thoroughly mixing 10 g of silica having a surface area of 300 m^2g^{-1} with 20 ml of nickel nitrate solution containing 2 g of nickel. The resulting material was dried overnight in air at 110°C.

A series of supported nickel catalysts and bulk nickel oxide were reduced in hydrogen at 450°C. for one hour prior to the introduction of a CO-H_2 feed at a temperature of 205°C. The enhanced activity of the TiO_2-supported nickel catalysts relative to a variety of other nickel catalysts is shown in Table IV. The 10% Ni/TiO_2 catalyst is much more active on a per gram of catalyst basis than other nickel catalysts containing much larger quantities of nickel.

TABLE IV

ACTIVITIES OF NICKEL CATALYSTS FOR CO-H_2 REACTION

(CO-H_2 Reaction Conditions: 205°C, 103, kPa, H_2/CO = 3)

Catalyst (a)	*μ Moles CO Converted/Sec/ Gram Nickel*	*μ Moles CO Converted/Sec/ Gram Catalyst*
5% Ni/η-Al_2O_3	3.44	0.172
8.8% Ni/η Al_2O_3	1.63	0.143
42% Ni/α-Al_2O_3	0.21	0.088
16.7% Ni/SiO_2	2.36	0.394
20% Ni/graphite	0.064	0.082
Bulk Ni Metal	0.032	0.032
10% Ni/TiO_2	22.8	2.28
1.53% Ni/TiO_2	8.35	0.113

(a) All catalysts reduced 1 hr. at 450°C. prior to activity test.

TiO_2 or titanium-containing oxide-supported nickel catalysts also exhibit desirable selectivity characteristics compared to bulk nickel or nickel on SiO_2 or Al_2O_3 supports. This is demonstrated in Table V. Nickel on a variety of supports, e.g. Al_2O_3, SiO_2, graphite and bulk nickel produce methane almost exclusively with only small amounts of hydrocarbons with carbon chain lengths up to 4. The TiO_2 or titanium-containing oxide-supported nickel catalysts show a large reduction in methane make and increase in paraffin products with carbon chain lengths of two carbon atoms and higher. This is especially desirable for the production of storable liquid fuels from CO-H_2 mixtures obtained from coal gasification.

The increased selectivity of TiO_2 or titanium-containing oxide-supported nickel catalysts is maintained over a range of conversions up to ~50% as demonstrated in Figure 1. Nickel catalysts prepared from other supports, however, show much poorer selectivity to high molecular weight paraffins than TiO_2 or titanium-containing oxide-supported metal catalysts.

The selectivity of the TiO_2 or titanium-containing oxide-supported nickel catalysts to hydrocarbons with carbon chain lengths of 2 and higher is also maintained at higher pressures compared to nickel on other supports. This is demonstrated in Table VI. The behavior of the Ni/TiO_2 catalysts as a function of pressure for the production of higher molecular weight paraffins is opposite to that of Ni/Al_2O_3. As Table VI shows it is most desirable to run the Ni/TiO_2 catalysts at low pressures to maximize production of higher molecular weight paraffins whereas high pressures are necessary for Ni/Al_2O_3. This is a desirable characteristic of TiO_2 or titanium-containing oxide-supported nickel catalysts since no compression of the synthesis gas would be required to operate a gasification-liquid fuels synthesis plant to maximize production of the desirable paraffin liquids.

Example 3

The advantage of TiO_2 or titanium-containing oxide-supported nickel catalysts in suppressing the formation of nickel carbonyl in the presence of CO was demonstrated using infrared spectroscopy. Nickel is known to react with carbon monoxide to form volatile nickel carbonyl $Ni(CO)_4$ which can result in a loss of nickel from the catalyst and the production of a poisonous effluent, i.e. $Ni(CO)_4$. The formation of $Ni(CO)_4$ is suppressed on TiO_2 or titanium-containing oxide-supported nickel catalysts compared to nickel on other supports such as Al_2O_3, SiO_2, and graphite.

The rate of $Ni(CO)_4$ formation from a 10% Ni/TiO_2 catalyst was compared to that from a 10% Ni/SiO_2 catalyst. The 10% Ni/SiO_2 catalyst was prepared by thoroughly mixing 10 g of SiO_2 having a surface area of 300 m^2g^{-1} with 22 ml of nickel nitrate solution containing 1.11 g nickel. The resulting material was dried in air at 120°C. overnight.

The 10% Ni/TiO_2 and 10% Ni/SiO_2 were, in separate experiments, pressed into thin wafers weighing 27-29 milligrams and charged to a cell identical to that described by D.J.C. Yates, W.F. Taylor and J.H. Sinfelt, J. Am. Chem. Soc., *86*, 2996 (1964). The air was evacuated from the cell and hydrogen flow initiated through the cell at 12 1/hr. The cell was rotated so that the wafer was at the silica end of the cell which was then inserted into a furnace. The wafers were reduced in hydrogen for 1 hour at 500°C. and evacuated for 10 min. at the same temperature to remove hydrogen. The wafers were then cooled in vacuum to room temperature and the cell rotated so that the infrared windows were in the spectrometer beam. The wafers in these experiments were kept out of the infrared beam so that the formation of $Ni(CO)_4$ in the gas phase could be monitored by infrared spectroscopy.

CO was added to each catalyst at a pressure of 1.87 kPa and the concentration of $Ni(CO)_4$ in the gas phase due to reaction of CO with nickel in the catalysts was followed as a function of time. Figure 2 shows a plot of the optical density of $Ni(CO)_4$ which is proportional to the concentration of $Ni(CO)_4$ in the gas phase around the catalyst as a function of time. The 10% Ni/TiO_2 catalyst is seen to be much less reactive toward $Ni(CO)_4$ formation than nickel on SiO_2. The TiO_2 and titanium-containing oxide-supported nickel catalysts thus have the desirable property of inhibiting the formation of $Ni(CO)_4$.

TABLE V

SELECTIVITY OF NICKEL CATALYSTS

$P = 103$ kPa, $H_2/CO = 3$

			Mole % Paraffin of each Carbon Number				
Catalyst	*T °C*	*% CO Conversion*	C_1	C_2	C_3	C_4	C_5^+
10% Ni/TiO_2	243	24	50	9	25	8	9
1.5% Ni/TiO_2	251	13.3	58	14	12	8	7
Bulk Ni	252	7.9	94	6	—	—	—
42% $Ni/\alpha\text{-}Al_2O_3$	236	2.1	76	14	5	3	1
8.8% $Ni/\eta\text{-}Al_2O_3$	230	3.1	81	14	3	2	—
5% $Ni/\eta\text{-}Al_2O_3$	254	10.8	90	7	3	1	—
16.7% Ni/SiO_2	220	3.3	92	5	3	1	—
20% Ni/graphite	234	24.8	87	7	4	1	—

TABLE VI

SELECTIVITY OF NICKEL CATALYSTS AT VARIOUS PRESSURES

(Reaction Conditions: $H_2/CO = 3$, T = 200-206°C)

			Mole % Product				
Catalyst	*Pressure (ATM)*	*% CO Conversion*	C_1	C_2	C_3	C_4	C_5^+
10% Ni/TiO_2	1	4	50.5	21.5	7.5	7.5	12
	10	3.5	56	37	5.5	1.5	—
	20	4.5	57.5	35	5.5	2	—
31.4% Ni/α-Al_2O_3	1	2.1	80	16	4	1	—
	10	1.9	69	29	2	—	—
	20	1.3	69	31	—	—	—

1 ATM = 103 kPa

EXAMPLE 4

Rhodium catalysts with improved selectivity to hydrocarbons with carbon chain lengths of two to five carbon atoms and improved selectivity to olefinic hydrocarbons in this carbon number range are obtained by depositing rhodium on TiO_2 and other titanium-containing oxide supports. Thus a 2 wt.% Rh/TiO_2 catalyst is prepared by stirring together 20 grams of TiO_2 with 4.08 ml of $RhCl_3$ solution containing 0.408 grams of rhodium. The TiO_2 was prepared by the flame hydrolysis of $TiCl_4$ and had a surface area of 60 m^2g^{-1}. Titania prepared by other techniques such as precipitation and calcination of a suitable salt is also satisfactory. After thoroughly mixing the TiO_2 and rhodium solution the mixture is dried in air at 120°C overnight.

To illustrate the desirable characteristics of Rh/TiO_2 it was compared to rhodium dispersed on Al_2O_3. Thus a 2% Rh/Al_2O_3 catalyst was prepared by mixing 5 grams of Al_2O_3 with 3.52 ml of $RhCl_3$ solution containing 0.102 grams of rhodium. The resulting mixture was dried in air at 110-120°C. overnight.

Table VII illustrates the desirable characteristics of TiO_2 or titanium-containing oxide-supported rhodium catalysts. The Rh/TiO_2 shows improved selectivity to hydrocarbons with carbon chain lengths of two to five hydrocarbons at all H_2/CO ratios. Thus, at an H_2/CO ratio of 1.6, 26 mole % of the products are C_2-C_5 hydrocarbons whereas Rh/Al_2O_3 produces only 14 mole % hydrocarbons in this carbon number range. Rh/TiO_2 also shows increased selectivity to olefins compared to Rh/Al_2O_3. As Table VII demonstrates, the ratio of ethylene the ethane is greater at all conditions for Rh/TiO_2 compared to Rh/Al_2O_3. Rh/TiO_2 thus exhibits the desirable characteristics of improved selectivity to C_2-C_5 hydrocarbons and olefins, these hydrocarbons being highly desirable as chemical intermediates for the production of plastics, rubbers, alcohols, ketones, aldehydes, esters and acids.

Table VII

Selectivities of Rhodium Catalysts

(Reaction Conditions: Pressure = 100 kPa)

				Mole Product %						
Catalyst (a)	*Temp. (°C)*	*% CO Conv.*	$\frac{H_2}{CO}$	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^+
2% Rh/TiO$_2$	248	0.3	0.6	63	7	0	19	12	0	0
		1.3	1.6	74	3	2	14	5	1	0
		3.3	3.0	80	2	3	11	3	2	0
		5.3	6.0	86	1	4	7	2	1	0
2% Rh/Al$_2$O$_3$	265	1.6	0.6	74	2	14	6	3	1	0
		3.5	1.6	85	0	10	3	11	0	0
		5.2	3.0	90	0	8	2	11	0	0
		13.9	6.0	93	0	5	2	1	0	0

(a) Each catalyst reduced 1 hour at 450°C before feed introduced at reaction temperature.

WHAT WE CLAIM IS:-

1. A process for the synthesis of hydrocarbons comprising passing H_2 and CO at a H_2/CO ratio of 0.1 to 10 over a catalyst or ruthenium, nickel or rhodium supported on a titanium-containing oxide at a space velocity of up to 50,000 V/V/Hr. and 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 hydrocarbon products in the desired ratio.

2. The process of claim 1 wherein the titanium-containing oxide is selected from TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanate, alkali titanates and rare earth titanates.

3. The process of claim 1 or claim 2 wherein the titanium-containing oxide is TiO_2.

4. The process of any one of claims 1 to 3 wherein the titanium-containing oxide has a surface area of from 1 to 200 m^2g^{-1}.

5. The process of claim 3 or claim 4 wherein the TiO_2 has a surface area of from 25 to 100 m^2g^{-1}.

6. The process of any one of claims 1-5 wherein the catalyst of ruthenium supported on a titanium-containing oxide has a ruthenium concentration of from 0.01 to 15 wt.% and a ruthenium particle crystallite size of from 1 to 20 nm.

7. The process of any one of claims 1-6 wherein the catalyst of ruthenium supported on a titanium-containing oxide has a surface area of from 10 to 60 m^2g^{-1}.

8. The process of any one of claims 1-5 wherein the catalyst of nickel supported on a titanium-containing oxide has a nickel concentration of from 0.01 to 75 wt.% and a nickel particle crystallite size of from 1-30 nm.

9. The process of any one of claims 1-5 wherein the catalyst of rhodium supported on a titanium-containing oxide has a rhodium concentration of from 0.01 to 10 wt.% and a rhodium particle crystallite size of from 1 to 20 nm.

10. The process of any one of claims 1 to 7 wherein the catalyst of ruthenium supported on a titanium-containing oxide has a ruthenium particle crystallite size of less than 5 nm.

11. The process of any one of claims 1 to 5 or 8 wherein the catalyst of nickel supported on a titanium-containing oxide has a nickel particle crystallite size of less than 10 nm.

12. The process of any one of claims 1 to 5 or 9 wherein the catalyst of rhodium supported on a titanium-containing oxide has a rhodium particle crystallite size of less than 5 nm.

13. A process for the synthesis of hydrocarbons according to any one of claims 1 to 12 substantially as hereinbefore described.

14. Hydrocarbons synthesized by a process according to any one of claims 1 to 13.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

FIGURE 1

SELECTIVITY VERSUS CONVERSION FOR NICKEL CATALYSTS

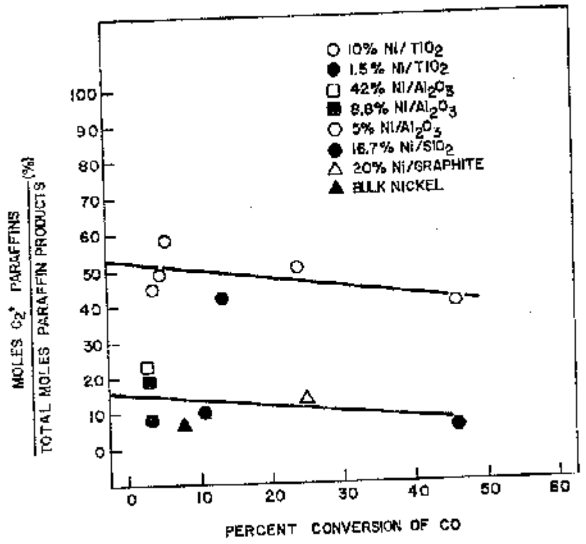

FIGURE 2

RATE OF NICKEL CARBONYL FORMATION OVER NICKEL CATALYSTS