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54 **Process for hydrocarbon synthesis catalyzed by cobalt on titania, enhanced by water addition.**

57 The addition of water into a Fisher-Tropsch hydrocarbon synthesis reaction zone employing a catalyst comprising promoted or unpromoted cobalt supported on titania results in increased CO conversion and C₅ + hydrocarbon production and a decrease in methane production. A preferred catalyst promoter is rhenium.

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**WATER ADDITION FOR INCREASED CO/H₂ HYDROCARBON SYNTHESIS ACTIVITY OVER CATALYSTS
COMPRISING RHENIUM PROMOTED COBALT ON TITANIA**BACKGROUND OF THE INVENTIONSUMMARY OF THE INVENTION

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It has now been discovered that in a Fischer-Tropsch hydrocarbon synthesis reaction for producing C₅ + hydrocarbons from a gaseous feed mixture of H₂ and CO in the presence of a catalyst comprising cobalt supported on titania, one can increase both the CO conversion activity and the C₅ + hydrocarbon selectivity and, at the same time, decrease the methane make by adding H₂O to the reaction zone. Thus, the present invention relates to a Fischer-Tropsch process for synthesizing C₅ + hydrocarbons by introducing into a catalytic reaction zone a feed mixture of CO, H₂, and H₂O wherein said feed contacts a catalyst comprising cobalt supported on TiO₂ at elevated temperature and for a time sufficient to convert at least a portion of said feed to C₅ + hydrocarbons. By cofeeding H₂O into the reaction zone, along with the H₂ and CO, it has been found that C₅ + hydrocarbon production is increased, CO conversion is increased and CH₄ production is decreased. The cobalt/titania catalyst may be promoted with one or more suitable promoter metals, such as rhenium.

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The H₂O that is added to the reaction zone may be in the form of steam or moisture or a suitable H₂O precursor, such as C₁-C₆ alcohols, for forming H₂O in-situ in the reaction zone. It is essential to the understanding of the process of this invention that the H₂O introduced into the reaction zone is external H₂O and not that H₂O which is formed in-situ in the reaction zone as a consequence of the Fischer-Tropsch hydrocarbon synthesis reaction from the H₂ and CO. It has also been found that the process of this invention improves with increasing pressure in the reaction zone and with decreasing CO conversion.

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25 DETAILED DESCRIPTION

The process of the present invention resides in adding, to the Fischer-Tropsch reaction zone, H₂O or a suitable H₂O precursor such as an alcohol. The amount of H₂O added to the reaction zone will range from 1-70 volume % of the total feed mixture of H₂O, CO and H₂ and, preferably, from 5-30 volume %. As the extent of CO conversion increases, the amount of water produced in-situ in the reaction zone increases and, concomitantly the beneficial effect of introducing additional water into the reaction zone to increase CO conversion, reduce CH₄ selectivity and increase C₅ + hydrocarbons selectivity decreases. Thus, in some cases, it may be advantageous to practice the process of this invention CO conversion levels below 60 percent. That is, below 60% per pass, reaction zone or stage. As the pressure in the reaction zone increases, the beneficial effect of the process of this invention of adding water to the reaction zone increases with respect to increasing CO conversion activity, decreased CH₄ selectivity and increased C₅ + hydrocarbon selectivity. At relatively low pressures in the reaction zone (i.e., less than 1 atmosphere), little effect will be seen in increased conversion activity, etc. by adding H₂O to the reaction zone. Thus, the process of this invention will be operated at a pressure above one atmosphere. In general the pressure will range from 1-50 atmospheres, and more preferably 5-30 atmospheres.

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In the process of this invention, the addition of H₂O enhances the formation of C₅ + hydrocarbons and reduces CH₄ make in a uni-directional or linear fashion. It has also been found that the water addition of the process of this invention enhances olefin formation. Further, it has been found that the rate of the Fischer-Tropsch reaction employing the process of this invention increases with increasing partial pressure of H₂O at any fixed total pressure in the reaction zone, up to a point, after which point the rate slowly goes down with continually increasing H₂O partial pressure. As an illustrative, but non-limiting example, in a plug flow reactor operated at 200 °C and 20 atmospheres of synthesis gas pressure, with a H₂/CO ratio of 2 and at low CO conversion conditions using a rhenium promoted cobalt/TiO₂ catalyst, the inlet H₂O partial pressure was systematically varied from 0 (no external H₂O addition) to 21 atmospheres. The productivity of the catalyst increased with increasing H₂O pressure up to the point when the H₂O pressure reached about 7 atmospheres, where a 3 fold higher activity was observed as compared with the base case without H₂O addition. Further increase in H₂O pressure induced a gradual decrease in activity and eventually, at an H₂O partial pressure of 21 atmospheres, the productivity was only 50% higher than the base case with no external water addition.

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In general, the Fischer-Tropsch hydrocarbon synthesis reaction process of this invention is carried out at a H₂:CO mole ratio of greater than 0.5, and preferably the H₂:CO mole ratio ranges from 0.5 to 6, more preferably from 0.5 to 3, at gas hourly space velocities ranging from 100 V/Hr/V to 5000 V/Hr/V, preferably from 300 V/Hr/V to 1500 V/Hr/V, at temperatures ranging from 150 °C to 300 °C, preferably from 180 °C to 240 °C, and pressures above 1 atm., preferably ranging from 1 atm. to 50 atm., more preferably from 5 atm. to 40 atm. and still more preferably from 5-30 atmospheres. In its most preferred form, a bed of catalyst comprised of from 5 percent to 15 percent cobalt, containing a suitable promoter such as rhenium in an amount sufficient to provide a catalyst containing rhenium:cobalt in ration ranging from 0.025:1 to 0.10:1, is dispersed on titania, preferably a high purity titania, and a bed of such catalyst is contacted with a gaseous admixture of carbon monoxide and hydrogen, or compound decomposable in-situ within the bed to generate carbon monoxide and hydrogen.

As previously stated, the hydrocarbon synthesis process of this invention employs a catalyst comprising cobalt supported on TiO₂. The catalyst will be a particulate catalyst composition containing a catalytically active amount of cobalt. The cobalt may, if desired, be promoted with one or more suitable promoter metals. In one embodiment, the promoter metal will be selected from the group consisting of Re, Hf, V, Nb, Ta, Cu, Zn, the lanthanide series elements or mixture thereof. Preferably the promoter will comprise Re alone or with one or more of the aforementioned elements. The promoter, if used, will be added to the catalyst in an amount to form a catalyst having a promoter:cobalt weight ratio greater than 0.010:1, preferably from 0.025:1 to 0.10:1. In terms of absolute concentrations, from 0.05 percent to 3 percent of rhenium, preferably from 0.15 percent to 1 percent of promoter, based on the total weight of the catalyst composition (dry basis), is dispersed with the catalytically active amount of cobalt on a titania support. In terms of absolute of concentrations, cobalt is present in the composition in amounts ranging from 2 percent to 25 percent, preferably from 5 percent to 15 percent, based on the total weight of the catalyst composition (dry basis), and sufficient promoter, such as rhenium, is added to form a catalyst having a weight ratio of rhenium:cobalt greater than 0.010:1, preferably from 0.025:1 to 0.10:1, based on the total weight of the cobalt and rhenium contained in the catalyst composition (dry basis). The absolute concentration of each metal will, of course, be preselected to provide the desired ratio of rhenium:cobalt as heretofore expressed.

The promoted or unpromoted cobalt/titania catalysts useful in the practice of this invention may be prepared by various techniques well known to those skilled in the art. In general, the cobalt or cobalt and promoter metal, will be deposited or impregnated onto a previously pilled, pelleted, beaded, extrudated or sieved titania support material by the impregnation method which also includes the incipient wetness technique. The procedure set forth below, although specifically directed to rhenium as the promoter metal, also applies to other promoter metals and mixtures of promoter metals.

In preparing a rhenium promoted catalyst, the cobalt and rhenium metals are deposited from solution onto the support material in preselected amounts in order to provide the desired amounts of cobalt and rhenium metals and weight ratio of the respective metals of cobalt and rhenium and the metal loading of the catalytic metals onto the titania support. In one method, the cobalt and rhenium are composited with the titania support material by contacting the support with a solution of a cobalt-containing compound, or salt, or a rhenium-containing compound, or salt, e.g., a nitrate, carbonate or the like. The cobalt salt or precursor may first be impregnated on the support followed by impregnation of the rhenium salt or compound or they may be impregnated simultaneously. The cobalt and rhenium precursor compounds used in the impregnation can be any organometallic or inorganic compounds which decompose to give cobalt and rhenium oxides upon calcination, such as a cobalt or rhenium nitrate, acetate, nitrite, carbonate, acetylactonate, naphthenate, carbonyl, or the like. The amount of impregnation solution used should be sufficient to completely wet or immerse the support material, usually within the range from 1 to 20 times of the carrier by volume, depending on the metal, or metals, concentration in the impregnation solution.

The impregnation treatment can be carried out under a wide range of conditions including ambient or elevated temperature. Metal components other than cobalt and rhenium can also be added. The introduction of additional promoter metal, or metals, into the catalyst can be carried out by any method and at any time of the catalyst preparation, for example, prior to, following or simultaneously with the impregnation of the titania support with the cobalt and rhenium components.

The catalyst precursor formed by impregnation of the titania support material by the catalytic metal components, will be dried by heating at a temperature above 30 °C, preferably above 125 °C, in the presence of a suitable atmosphere such as air, nitrogen, oxygen, etc. or under vacuum. It is necessary to calcine the catalyst precursor composite prior to use in order to convert the rhenium and cobalt to their respective oxides. Thus, the catalyst precursor composite will be contacted with oxygen, air, or other oxygen-containing gas at a temperature sufficient to oxidize the rhenium and cobalt and convert same to their respective oxides. This may be done at temperatures above 150 and preferably above 200 °C.

However, temperatures up to 500 °C may also be used to form, and if necessary, regenerate a severely deactivated catalyst.

In general, the catalyst precursor will be calcined at temperatures ranging from 150 to 300 °C. After the catalytic metals have been oxidized, the cobalt and rhenium oxides contained on the catalyst must then be reduced to form the final catalyst composition useful in the process of this invention. This reduction is accomplished by contacting the catalyst, whether or not previously oxidized, with a suitable reducing gas such as hydrogen or a hydrogen-containing gas stream at elevated temperatures above 250 °C and preferably above 300 °C. Generally the catalyst is calcined ranging from 250 to 500 °C and preferably from 300 to 450 °C for periods ranging from 1/2 to 24 hours at pressures ranging from ambient to 40 atmospheres.

The invention will be more readily understood by reference to the examples below.

EXAMPLES

Example 1 - 12% Co/TiO₂

High purity (Co(NO₃)₂ · 6H₂O (99.999% purity puratronic grade, 25.0 grams) was dissolved in 18 cc of spectroscopic grade acetone and this solution was added dropwise, while stirring, to 37 grams of rutile TiO₂ (80-140 mesh, BET = 11 m²/g). The resulting material was dried overnight at 90 °C, followed by calcination in air at 250 °C for 16 hours. Reduction was carried out in H₂ (500 scm³/m, 1 atm) by increasing the temperature to 450 °C over a period of 4 hours and then keeping at 450 °C for 16 hours. The reduced catalyst was then passivated at 25 °C using a 1% O₂ - 99% He mixture. Chemisorption measurements showed that this Co/TiO₂ catalyst had 2.9% dispersion (2.9% of the Co was exposed).

The performance test of this catalyst was carried out by charging an intimate mixture of the said 12% Co/TiO₂ catalyst (3.0 grams) and a diluent (low-surface-area rutile, 80-140 mesh, 18 grams) into a down-flow fixed bed reactor made of 3/8" OD stainless steel tube with a concentric 1/8" OD thermocouple well. The use of diluent and an aluminum block jacket fitted tightly around the reactor minimized uneven temperature profile along the bed. The catalyst was then rereduced in a flowing H₂ stream (200 cc/m, 1 atm) overnight at 450 °C, cooled to 175 °C and then pressurized to 20 atm using a pre-mixed gas composed of 63.9% H₂, 32.1% CO and 4.0% N₂. At pressure and at a preset flow rate, the temperature was raised to 200 °C over a period of one hour and then data acquisition was initiated. The rate of CO conversion and the rates of various hydrocarbon products formation were monitored using two on-line GC's. The data taken after 70 hours on-stream-time are shown in Table 1.

TABLE 1

EFFECTS OF ADDED H ₂ O ON ACTIVITY AND SELECTIVITIES OF CO HYDROGENATION OVER 12% Co/TiO ₂				
Total Pressure = 20.7 atm.				
Feed Gas Composition = 63.9% H ₂ /32.1% CO/4.0% N ₂				
Temperature = 200 °C				
	Run 1	Run 2	Run 3	Run 4
SV, SCM ³ /g.hr ^{*1}	3540	3540	1180	1180
% H ₂ O added ^{*2}	0	12	0	35
% CO Conversion	8.5	21.9	40.2	50.7
CH ₄ Selectivity ^{*3}	9.6	4.1	6.5	2.7
CO ₂ Selectivity ^{*3}	0.22	0.21	0.15	0.68
1-Olefin/Paraffin Ratios				
C ₂	0.22	0.78	0.11	0.47
C ₃	2.22	3.92	1.61	3.29
C ₄	1.24	2.38	0.84	2.00
Hydrocarbon Product Distribution, wt. %				
CH ₄	10.9	4.6	7.5	3.1
C ₂ -C ₄	9.8	5.0	8.1	4.7
C ₅ -C ₉	15.9	9.3	13.2	10.5
C ₁₀ +	63.4	81.1	71.2	81.6
C ₅ +	79.3	90.4	84.4	92.1

*1 cc of H₂ and CO measured at 1 atm., 22 °C per gram of catalyst per hour.

*2 Moles of H₂O added per 100 moles of CO and H₂.

*3 Moles of CH₄ or CO₂ produced per 100 moles of CO converted.

Comparison of the data with and without the external H₂O addition (Run 2 vs. Run 1 and Run 4 vs. Run 3) clearly establishes the advantages of H₂O addition; (1) the productivity increases markedly (up to 2.5 fold increase), (2) the olefin selectivity increases as exemplified by the large increases in 1-olefin/paraffin ratios in the C₂-C₄ fractions and (3) the desired heavy hydrocarbon product yields, which may be gauged by the products of the Co conversion level and C₁₀ + selectivity, increase dramatically.

Thus, this example clearly demonstrates the benefits of conducting a Fischer-Tropsch hydrocarbon synthesis reaction with external H₂O addition in the presence of a catalyst comprising cobalt supported on titania.

Example 2 - 12% Co-0.5% Re/TiO₂

This example demonstrates the benefits of external H₂O addition when Fischer Tropsch hydrocarbon synthesis reactions are carried out using promoted Co/TiO₂ catalysts. This example specifically shows that the benefits of external H₂O addition demonstrated in Example 1 for Fischer-Tropsch synthesis over a Co/TiO₂ catalyst are not diminished by addition of a promoter, or promoters, to the base catalyst, Co/TiO₂, as exemplified by the beneficial effects of external H₂O addition to a rhenium promoted Co/TiO₂ catalyst.

109 grams of Co(NO₃)₂·6H₂O and 16 cc of aqueous perrhenic acid containing 0.83 g of rhenium (as metal) were dissolved in 300 cc acetone, to which 160 g of TiO₂ (rutile, BET = 13.6 ²/g, 80-140 mesh) was added. The acetone was then removed in a rotary evaporator, followed by further drying at 140 °C in a vacuum. The resulting material was calcined in air at 250 °C for 3 hours. 3 g of this catalyst was intimately mixed with 12 g of diluent (low-surface-area rutile, 80 - 140 mesh) and charged to the reactor as described in the previous example. The catalyst was then reduced in-situ in flowing H₂ (1 atm, 200 cc/m) by gradually raising the temperature from room temperature to 450 °C over a period of 4 hours and then keeping at 450 °C for 16 hours. The performance data, listed in Table 2, were taken after 200 hours on-stream-time.

TABLE 2

EFFECTS OF ADDED H ₂ O ON ACTIVITY AND SELECTIVITIES OF CO HYDROGENATION OVER RHENIUM PROMOTED Co/TiO ₂ (12% Co - 0.5% Re/TiO ₂)					
Total Pressure = 20.7 atm. Feed Gas Composition = 64% H ₂ /32% CO/4% N ₂ Temperature = 200 ° C					
	Run 5	Run 6	Run 7	Run 8	Run 9
SV, SCM ³ /g.hr	3510	3510	3510	2340	2340
% H ₂ O added	0	12	26	0	18
% CO Conversion	9.9	24.2	26.4	21.0	36.3
CH ₄ Selectivity	9.4	4.3	3.4	8.1	3.6
CO ₂ Selectivity	0.39	0.38		0.27	0.38
1-Olefin/Paraffin Ratios					
C ₂	0.34	0.48	0.63	0.22	0.56
C ₃	2.42	3.16	3.34	2.22	3.26
C ₄	1.71	1.97	2.39	1.24	1.97
Hydrocarbon Product Distribution, wt%					
CH ₄	10.7	4.9	3.9	8.8	4.3
C ₂ -C ₄	8.4	4.2	3.6	5.9	4.0
C ₅ -C ₉	15.0	8.9	7.5	10.3	7.9
C ₁₀ +	65.9	82.0	85.0	75.0	83.8
C ₅ +	80.9	90.9	92.5	85.3	91.7

The results in Table 2 clearly establish that the benefits of external H₂O additions on the activity/selectivities of a rhenium-promoted Co/TiO₂ catalyst are comparable to those described in Example 1. This example thus establishes that promoted Co/TiO₂ catalysts show higher productivity and better product selectivities when external H₂O addition is performed during the Fischer-Tropsch hydrocarbon synthesis reaction.

Example 3

A series of runs to examine the influences of process variables, including the levels of externally added H₂O, were conducted using the catalyst and procedure described in Example 2, except that the catalyst used in this example was 25% less active than that described in Example 2 due to different histories. The results in Table 3 nevertheless demonstrate that the beneficial effects of external H₂O addition can be realized both at a relatively low addition level of 6.7% and at a very high level of 104%. Thus, this example demonstrates that for a wide range of external H₂O addition levels, 2-100% based on the combined H₂ and CO feeds, beneficial effects of increased productivity and desirable selectivities can be realized. The results in Table 3 also demonstrate that the beneficial effects of added H₂O do not vary significantly over the temperature ranges of 180-220 ° C, which suggests that the effects of external H₂O addition do not vary significantly with process conditions.

TABLE 3

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EFFECTS OF ADDED H ₂ O ON ACTIVITY AND SELECTIVITIES OF CO HYDROGENATION OVER RHENIUM PROMOTED Co/TiO ₂					
Sum of Partial Pressures of CO and H ₂ = 20.0 atm					
Feed Gas Composition = 64.2% H ₂ /31.8% CO/4.0% N ₂					
Run #	SV SCM ³ /g.hr	Temperature °C	% H ₂ O Added	% CO Conversion	CH ₄ Selectivity
10	3650	200	0	5.2	13.0
11	3650	200	6.7	13.7	5.8
12	3650	200	28.0	18.8	4.1
13	3650	200	34.0	15.8	3.3
14	3650	200	104.0	7.7	2.9
15	10950	221	0	5.7	16.2
16	10950	221	25.5	13.9	7.4
17	1210	181	0	8.2	9.0
18	1210	181	23.5	25.4	2.2

Claims

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1. A process for synthesizing C₅ + hydrocarbons from a feed comprising a mixture of H₂ and CO which comprises introducing said feed and H₂O into a reaction zone wherein they contact, at elevated temperature of at least 100 °C and for a time sufficient to convert at least a portion of said feed to C₅ + hydrocarbons, a catalyst comprising cobalt supported on titania.
 2. The process of claim 1 wherein the amount of water introduced into said reaction zone with said feed ranges from 1 to 70 volume % of the total amount of H₂O, CO and H₂ introduced into said reaction zone.
 3. The process of claim 1 or claim 2 wherein said reaction occurs at a pressure above 1 atmosphere.
 4. The process of any one of claims 1 to 3 wherein said catalyst is promoted with one or more promoter metals.
 5. The process of claim 4 wherein said promoter metal is selected from the group consisting of Re, Hf, V, Nb, Ta, Cr, Zn, lanthanide elements or mixtures thereof.
 6. The process of claim 4 or claim 5 wherein said catalyst contains rhenium promoter metal.
 7. The process of claim 6 wherein the amount of rhenium present in said catalyst composition is greater than 0.01 to 1.
 8. The process of any one of claims 1 to 7 wherein said reaction temperature is at least 150 °C.
 9. The process of any one of claims 1 to 8 wherein the mol ratio of H₂ to CO in the feed ranges from 0.5 to 6.
 10. The process of any one of claims 1 to 9 wherein the amount of cobalt present in said catalyst composition ranges from 2 to 25 wt.% of the total catalyst composition.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	FR-A-2 388 782 (SHELL) * claims 1-11,13 * ---	1-5,8-10	C 07 C 1/04 B 01 J 23/74
Y	US-A-4 595 703 (VIRGIL L. PAYNE et al.) * claims 1-3, 6-9, 13-18 * ---	1-5,8-10	
Y	EP-A-0 109 702 (SHELL) * claims 1,3-6; page 16-19 * ---	1-5,8-10	
A	EP-A-0 216 967 (EXXON) * claims 1,2,8,9 * ---	1,8-10	
A,P	EP-A-0 266 898 (EXXON) * claims 1-10 * -----	1-6,8-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 1/00 B 01 J 23/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22-06-1989	Examiner DIETRICH A.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			