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(54) Process for producing C2-C4 hydrocarbons from carbon monoxide and hydrogen.

(57) Hydrocarbons of two to four carbon atoms are prepared by an improved Fischer-Tropsch process, the improvement comprising the use of a catalyst comprising:

(A) At least one material selected from the group consisting of the sulfide, oxide or metal of Mo, W, Re, Ru and Pt;
(B) at least one material selected from the group consisting of the hydroxide, oxide or salt of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba and Th; and
(C) a support.

The catalyst demonstrates good C_2-C_4 selectivity, is resistant to sulfur poisoning and is regenerable.

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PROCESS FOR PRODUCING C_2-C_4 HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN

This invention relates to an improved process for the production of hydrocarbons from carbon monoxide and hydrogen. In one aspect, this invention relates to a catalyst for use in the process to produce hydrocarbons containing two to four carbon atoms.

The art contains many examples of metals known to be useful in reacting carbon monoxide with hydrogen to produce a variety of compounds -- both hydrocarbons and oxygenated compounds. These metals include, among others, Mo, W, Th, Ru, Re, Pt, Ni, Co, and Fe. It is upon the last three of these metals that most commercial experience is based. In the Fischer-Tropsch synthesis, carbon monoxide and hydrogen are reacted over an iron, nickel or cobalt catalyst to produce saturated and unsaturated hydrocarbons and oxygenated compounds containing from about one to as many as one thousand carbon atoms. The hydrocarbons can be aliphatic, alicyclic, or aromatic. Commercial utilization of this synthesis prior to 1950 was accomplished largely in Germany and is summarized in Storch, Columbic, and Anderson: The Fischer-Tropsch and Related Synthesis, John Wiley and Sons, New York 1951.

The following references are illustrative of the prior art and are helpful to an understanding of Applicant's invention:

Schultz, John Floyd, "Nobel Metals, Molybdenum and Tungsten in Hydrocarbon Synthesis", by J. F. Schultz, F. S. Carn, and R. B. Anderson. (Washington)

West German Patent No. 2,343,032 "Process for Controlling Fischer-Tropsch Synthesis", Inventor: Dr. Mark Eberhard Dry, Priority Date: September 5, 1972.

U.S. Patent 2,490,488 "Hydrocarbon Synthesis Catalyst", December 6, 1949.

As mentioned above, the most extensive commercialization of the Fischer-Tropsch synthesis has been with the use of either an iron, nickel or cobalt catalyst. Such catalysts produce a mixture of saturated and unsaturated aliphatic and aromatic hydrocarbons as well as oxygenated compounds, which for the most part contain more than four carbon atoms. The cracking of these compounds to produce ethylene and/or propylene is not very efficient. For this purpose the desired compounds are ethane, propane, and the various isomers of butane and butene. In addition sulfur impurities such as hydrogen sulfide, carbonyl sulfide, or any other sulfur compound deactivate iron and cobalt catalysts in concentrations as low as 0.1 ppm.

Schultz (cited above) has shown molybdenum to have some sulfur resistance. His work was directed toward the development of an efficient catalyst to produce methane from carbon monoxide and hydrogen and he was reasonably successful. However, methane is not the preferred feedstock for the production of ethylene and/or propylene. For the present purposes, the catalysts of iron and cobalt produce molecules containing too many carbon atoms, and the catalysts tested by Schultz produce molecules containing too few carbon atoms.

The present invention relates to a process which produces molecules containing a more desirable number of carbon atoms for use as ethylene cracker feedstocks. Typical catalysts in use today for this reaction require lowering of the concentration of sulfur impurities to approximately 0.1 ppm. Since it is expensive to decrease the concentration of sulfur impurities to a level of approximately 0.1 ppm, development of a catalyst usable at a higher concentration would result in considerable savings in investment and operating costs in a commercial facility. The catalyst of the present invention can be employed with a higher concentration of sulfur impurities in the feedstock. The catalyst of the present invention does not require precious metals and is capable of sustained operation at a hydrogen to carbon monoxide ratio of one to stimulate formation of the saturated and unsaturated hydrocarbons containing from two to four carbon atoms.

The present invention is a process for producing saturated and unsaturated hydrocarbons containing two to four carbon atoms by contacting carbon monoxide and hydrogen at reactive conditions, characterized by contacting the carbon monoxide and hydrogen with a catalyst consisting of:

(A) between 1 percent and 95 percent by weight based upon the weight of the catalyst of at least one material selected from the group consisting of the metal, oxide or sulfide of molybdenum, tungsten, rhenium, ruthenium and platinum;

(B) between 0.05 percent and 50 percent by weight based upon the weight of the catalyst of at least one material selected from the group consisting of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium and thorium; and

(C) at least 1 percent by weight based upon the weight of the catalyst of a support.

The catalyst of this invention is advantageous for producing hydrocarbons of two to four carbon atoms but is particularly advantageous for producing hydrocarbons of two or three carbon atoms, and especially advantageous for producing hydrocarbons of two carbon atoms.

The carbon monoxide required for the process can be obtained from any carbon source, such as from the degradation of coal or of high molecular weight hydrocarbon residuals. In the case of a carbon-supported sulfur-resistant catalyst species of the invention (the metals molybdenum, tungsten, and their oxides and sulfides), the feed can contain substantial quantities of sulfur impurities without irreversibly affecting either the selectivity or activity of the catalyst. The molar ratio of hydrogen to carbon monoxide ranges generally from at least about 0.25 and preferably about 0.5 to an upper limit of about 4.0 and preferably about 1.5.

The catalyst used in the practice of the invention is typically a three-component catalyst. The first component is at least one material selected from the group consisting of the sulfide, oxide or metal of molybdenum, tungsten, rhenium, ruthenium and platinum. "At least one" means that the first component can consist of two or more members of this enumerated group, including such combinations as the sulfide, oxide and metal of one element, or the oxides or sulfides of different elements, or the sulfide of one element and the oxide of another, or different oxides or sulfides, if any, of the same element, etc. As used herein, "sulfide" includes those compounds that have oxygen and sulfur directly attached to the same metal atom, such as O-Mo-S. This first component is present in an amount, based upon the weight of the catalyst, of at least about 1 and preferably at least about 10 weight percent with an upper limit of about 95 and preferably about 50 weight percent. A preferred first component is at least one material selected from the group consisting of the sulfide, oxide or metal of molybdenum and tungsten. An especially preferred first component is at least one material selected from the group consisting of the sulfide, oxide or metal of molybdenum.

The second component is at least one material selected from the group consisting of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium and thorium. "At least one" means that the second component can consist of two or more members of this enumerated group, including such combinations as the hydroxide, oxide and salt of one element, or the hydroxides, oxides or salts of different elements, or the hydroxide of one element and the oxide of another, or different oxides or salts, if any, of the same element, etc. The second component is present in an amount, based upon the weight of the catalyst, of at least about 0.05 and preferably at least about 0.5 weight percent with an upper limit of about 50 and preferably about 10 weight percent. A preferred second component is at least one material selected from the group consisting of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium and cesium. An especially preferred second component is at least one material selected from the group consisting of the hydroxide, oxide or salt of potassium.

The third component is a support of any physical form, such as granules, beads, extrudates, etc. Examplary supports include: alumina, silica, carbon, zirconia, magnesia, etc. The carbon supports include saran carbon beads. These beads are a substantially dust- and contaminant-free carbonized product made from vinylidene chloride polymers and, when loaded with the first two components of this invention's catalyst, constitute a novel Fischer-Tropsch catalyst having a pronounced selectivity for producing C_2-C_4 hydrocarbons. For more detail regarding these beads, see "The Absorption Characteristics of Polyvinylidene Chloride Carbon" by A. N. Ainscough, D. Dollimore, G. R. Heal in Carbon 11, 189-197 (1973). Based upon the weight of the catalyst, the support comprises at least about 1 percent of the catalyst and generally not more than about 98.95 percent of the catalyst. Preferably, the support comprises at least about 50 weight percent, and most preferably at least about 80 weight percent, of the catalyst.

Although any number of materials can serve as a support, alumina and carbon supports are preferred, with the latter especially preferred. The activity and selectivity of a catalyst comprising a carbon support is essentially equivalent to that comprising an alumina support. The activity of the catalyst is a measure of its ability to promote the formation of hydrocarbon molecules without regard to the number of carbon atoms in a molecule. The selectivity of the catalyst is a measure of it ability to promote the formation of hydrocarbon molecules containing the desired number of carbon atoms.

Components of this invention's catalyst can be present per se or as an integral part of one another or as a combination thereof. Illustrative of components being present as an integral part of one another, carbon supports prepared from coconut often contain relatively small (based on the weight of the support) amounts of alkali metal oxides and/or hydroxides.

Preferred species of this invention's catalyst have as a first component at least one of the sulfide, oxide or metal of molybdenum or tungsten. More preferred species have as a first component at least one material of the sulfide, oxide or metal of molybdenum or tungsten, and as a second component at least one of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium and cesium. Still more preferred species have as a first component at least one of the sulfide, oxide or metal of molybdenum or tungsten, as a second component at least one of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium and cesium, and as a third component an alumina or carbon support. Especially preferred species have as a first component at least one of the sulfide, oxide or metal of molybdenum, as a second component at least one of the hydroxide, oxide or salt of potassium, and as a third component a carbon support.

The presence of sulfur impurities in the feed alters the selectivity and activity of the catalyst after a period of time. Methane production is increased with a consequential decrease in production of hydrocarbons containing two or more carbon atoms. The sulfides and oxides of molybdenum and tungsten have been found resistant to poisoning by sulfur impurities. Regeneration of these sulfur resistant catalysts can be accomplished by treatment with hydrogen at about 15 psia and 400°C-600°C for about sixteen to forty-eight hours. Such treatment of a sulfur resistant catalyst restores the catalyst's activity and selectivity to its initial levels.

Reactive (process) conditions can vary over a rather broad range. The pressure can vary from about 15 psia (1.06 kg/cm^2) to about 2000 psia (141 kg/cm^2). The preferred pressure is generally between about 200 and about 1000 psia (14.1-70.5 kg/cm^2). The reaction temperature ranges from at least about 250°C and preferably about 375°C to an upper limit of about 500°C and preferably about 425°C.

The following examples illustrate the invention. Unless otherwise indicated, all parts and percentages are by weight.

Apparatus and Procedure:

In preparation of a catalyst, supports were impregnated by a technique known as the incipient wetness technique. Water-soluble salts of active components of the catalyst and a support were chosen. A quantity of water which a catalyst support will absorb is known as its pore volume. According to the desired catalyst loading, a quantity of the soluble salts was dissolved in water approximately equal to the pore volume of the support. The support was then immersed in the water which it absorbed completely. A wet cake was formed. The wet cake was first air-dried at room temperature for sixteen to twenty-four hours. It was then placed in an oven and heated at a rate of between about 0.4°C and about 1.8°C per minute in the presence of air or nitrogen to a final temperature dependent upon the type of support. Carbon supports were heated to between about 300°C and about 400°C. Alumina supports were heated to between about 500°C and about 650°C. Both supports were held at this final temperature for about six hours before being allowed to cool slowly to room temperature.

In Examples 1 through 6 an apparatus was utilized which included in sequential order three high-pressure gas bottles, a manifold, and five reactors each equipped on the downstream side with a fine metering valve and a rotameter through a sampling manifold to a gas chromatograph. The first bottle contained a mixture of hydrogen and carbon monoxide in a one to one molar ratio. The second bottle contained hydrogen and carbon monoxide in the same ratio but also contained carbonyl sulfide as a doped sulfur impurity. The third bottle contained hydrogen alone. Each bottle was independently connected to the manifold. The manifold was constructed such that any of the three bottles could be used either to feed all five reactors simultaneously, or to feed any one of the five alone, or to feed any combination of the reactors. Through the sampling manifold, the product of each reactor could be piped to the gas chromatograph for analysis.

The apparatus permitted reacting carbon monoxide and hydrogen in the presence of as many as five different catalysts under the same conditions. Before each run, catalyst was loaded in the reactors to be used and heated to 350°C over a four-hour period in the presence of hydrogen. The hydrogen flow and a temperature of 350°C were maintained for sixteen more hours. Then the catalyst was raised to a final temperature over a four--hour period. The final temperature was dependent upon the support as detailed above. This final temperature was held for sixteen to forty-eight hours. The outlet temprature of each reactor in use was maintained by the use of a hot air stream. The reactors were then lowered to operating temperature in the presence of hydrogen. Next, feed from the high-pressure gas bottle containing hydrogen and carbon monoxide was allowed to flow through the manifold to the reactor(s) being utilized. Pressure, flow, and temperature were adjusted to operating values.

The catalyst used in several runs was poisoned with a sulfur impurity and then reduced with hydrogen to determine its ability to be regenerated. This was the case in Examples 5 and 6, where, after a time period sufficient to establish the performance of the catalyst, the feed was switched from the bottle containing pure hydrogen/carbon monoxide to the bottle containing hydrogen/carbon monoxide with a sulfur impurity. After the effect on the catalyst of this impurity had been determined by reference to the carbon monoxide conversion and the product hydrocarbon distribution, the feed containing the impurity was shut off. For sixteen hours hydrogen was allowed to flow through the reactors which had been heated to a temperature between about 500°C and about 600°C. The feed of pure hydrogen/carbon monoxide was restored for a period of time sufficient to determine the performance of the catalyst. The feed was than shut off and while they cooled to ambient temperature the reactors were purged with hydrogen.

In Example 2, the gas bottle containing hydrogen and carbon monoxide was used exclusively. After a period of time sufficient to establish the performance of each of the four catalysts, the feed was shut off. The reactors were purged with hydrogen while cooling to ambient temperature.

Subscripts in all examples indicate the number of carbon atoms. All hydrocarbon analyses are given in carbon mole percent in all examples. "Carbon mole percent" is defined as one hundred times the moles of carbon present in a hydrocarbon fraction divided by the total moles of carbon in product hydrocarbon. If one mole of ethane and one mole of ethylene are found in the C_2 fraction, this is counted as four moles of carbon. The term "product hydrocarbon" excludes any carbon dioxide produced. Unless otherwise indicated, molybdenum concentrations are reported as MoO_3 equivalents and potassium concentrations are reported as K_2O equivalents.

Example 1:

Using the above catalyst, procedures, and apparatus, the following run was made to demonstrate the effect of the concentration of the second component of the catalyst upon product selectivity. The first component of the catalyst was molybdenum trioxide which was present in a concentration of 10 weight percent on a support of saran carbon beads. In Runs 1B and 1C, the second component of the catalyst was potassium hydroxide. Reaction conditions are summarized below.

Temperature	400°C
Pressure	315 psia (22.3 kg/cm^2)
Volume Hourly Space Velocity (VHSV)	300 hr^{-1}

The volume hourly space velocity is an indirect measure of the contact time between the catalyst and reactants. It is calculated by dividing the combined volume rate of flow of the reactants by the volume of the catalyst.

The catalyst of Run 1A contained no alkali, that of Run 1B contained 2.02 percent alkali (calculated as K_2O), and that of Run 1C contained 4.42 percent alkali (calculated as K_2O).

PRODUCT HYDROCARBON DISTRIBUTION

	Run 1A	Run 1B	Run 1C
C_1 Hydrocarbons	70.6	53.8	37.5
C_2 Hydrocarbons	22.4	28.1	30.8
C_3 Hydrocarbons	6.2	13.3	21.3
C_4 Hydrocarbons	0.8	3.6	7.3
C_5 Hydrocarbons	0	1.2	3.2
C_6 Hydrocarbons	0	0	0

Note the increased yield in C_2 and higher hydrocarbons as the alkali concentration increases from Run 1A to Run 1C. These data show the surprising and significant increase in hydrocarbons containing from two to four carbon atoms available through the invention.

Example 2:

The following runs were made at constant pressure, temperature, and volume hourly space velocity. Molybdenum trioxide, the first component of the catalyst, was utilized on saran carbon beads for all runs. The second component of the catalyst, the alkali metal carbonate, was different for each reactor. The apparatus of Example 1 was used. Saran carbon beads were loaded with approximately 10 weight percent MoO_3 and, in each case, an equimolar amount of the respective carbonate according to "Apparatus and Procedure". The loading is summarized below:

Second Component (Alkali Carbonate)	Millimoles Alkali Carbonate	Weight Percent Alkali (Calculated as alkali oxide)
Na_2CO_3	5.23	1.19
K_2CO_3	5.26	2.02
Rb_2CO_3	5.14	4.39
Cs_2CO_3	5.20	6.67

Reaction conditions for each of the four runs were the same as in Example 1.

Run 1A which utilized only the first component of the catalyst, is reproduced below for comparison purposes. Analysis of the product hydrocarbons revealed them to be composed of:

	Run 1A (First Component only)[1]	Run 2 (Second Component Utilized)[1] Na_2CO_3	K_2CO_3	Rb_2CO_3	Cs_2CO_3
C_1 Hydrocarbons	70.6	57.1	54.5	55.0	58.1
C_2 Hydrocarbons	22.4	27.9	28.7	30.5	27.3
C_3 Hydrocarbons	6.2	12.3	12.0	11.3	12.7
C_4 Hydrocarbons	0.8	2.7	3.5	3.2	1.9
C_5 Hydrocarbons	0	0	1.3	0	0

[1]All runs made with the catalyst on a saran carbon support.

These data show that the carbonates of Na, K, Rb, and Cs were satisfactory when used with molybdenum trioxide in the present invention to increase the yield of hydrocarbons containing from two to four carbon atoms. An average increase in yield of the desired hydrocarbons of about 50 percent was realized through the use of both components of the catalyst.

Example 3:

This example compares the effect of potassium carbonate loading on the selectivity of cobalt/molybdenum catalysts. A quantity of commercially-available catalyst was impregnated with potassium carbonate (as detailed under "Apparatus and Procedure Section" to a level of 4 weight percent (calculated as K_2O). This catalyst is a mixture of 4 weight percent cobalt oxide and 12 weight percent molybdenum trioxide on a support of alumina (80 weight percent). The apparatus of Example 1 was utilized. Reaction conditions are summarized below. The temperature was 412°C, the pressure 315 psia (22.3 kg/cm^2) and the VHSV 256 hr^{-1}.

The carbon monoxide conversion was found after several hours on stream to be 72 mole percent. The carbon monoxide conversion is defined as 100 times the moles of carbon monoxide converted divided by the moles of carbon monoxide in the feedstock. The reaction product consisted of:

C_1 Hydrocarbons	36.6%
C_2 Hydrocarbons	38.4%
C_3 Hydrocarbons	17.3%
C_4 Hydrocarbons	5.3%
C_5 Hydrocarbons	2.2%

For comparison, note this example from the work of Schultz, Carn, and Anderson of the U.S. Bureau of Mines (full cite above). Run Z375 on page 18 of their report most nearly approximates the conditions herein employed. In that case an unsupported cobalt/-molybdenum catalyst was used to react carbon monoxide and hydrogen under the following conditions:

Temperature	300°C
VHSV	300 hr^{-1}
H_2/CO Molar Ratio	2

Analysis of the product revealed:

C_1 Hydrocarbons	74.9%
C_2 Hydrocarbons	12.4%
C_3 and C_4 Hydrocarbons	9.9%
C_5 Hydrocarbons	2.8%

Analysis of these data reveal a surprising and significant improvement in the yield of C_2 to C_4 hydrocarbons. The yield of this fraction rose from about 25 percent in the case of the Bureau of Mines work to about 63 percent in the case of the catalyst of the instant invention.

Example 4:

In the following runs which utilized the apparatus of Example 1 and the catalyst impregnation procedures of the Apparatus and Procedure Section, all variables were held constant except for the second component of the catalyst. The catalyst used in Run 4A included only components one and three. The catalyst was 11.15 weight percent tungsten trioxide on a support of saran carbon. The catalyst used in Run 4B was comprised of 10 weight percent tungsten trioxide and 4 weight percent potassium oxide on a saran carbon support.

Reaction conditions for each run were:

Temperature	400°C
VHSV	300 hr^{-1}
Pressure	300 psia (21.2 kg/cm^2)

Analysis of the product revealed:

	Run 4A	Run 4B
C_1 Hydrocarbons	54.1	40.6
C_2 Hydrocarbons	28.6	40.5
C_3 Hydrocarbons	13.9	13.7
C_4 Hydrocarbons	2.7	5.2
C_5 Hydrocarbons	0.7	0

This example illustrates the significant increase (about 30 percent) in hydrocarbons containing two or more carbon atoms available through the invention while using tungsten as a component of the catalyst.

Example 5:

The following run was made with a catalyst of molybdenum trioxide and potassium oxide on alumina. Carbonyl sulfide was used to poison the catalyst to check the effect of hydrogen treatment upon activity and selectivity. Molybdenum trioxide and potassium oxide were impregnated on the alumina as under Apparatus and Procedure Section. Levels of treatment were:

Weight percent MoO_3	10
Weight percent K_2O	4

The apparatus of Example 1 was used and reaction conditions were:

Temperature	400°C
Pressure	300 psia (21.2 kg/cm^2)
VHSV	300 hr^{-1}

Conversions and product distributions at various times during the run are summarized below.

Time (Hours)	Carbon Monoxide Conversion (Mole Percent)	PRODUCT HYDROCARBON DISTRIBUTION (Mole Percent)					
		C_1	C_2	C_3	C_4	C_5	C_6
11.2	35.7	34.6	22.3	24.4	12.3	3.2	3.2
12	100 ppm carbonyl sulfide was added to the feed on a continuous basis.						
85	20.9	47.2	18.1	26.3	8.4	0	0
85.1	Carbonyl sulfide was eliminated from the feed. The feed was interrupted to treat the catalyst with hydrogen at 600°C for about sixteen hours.						
101	Feed restored.						
121	32.6	53.2	20.6	17.0	9.2	0	0

These data show that carbonyl sulfide at 100 ppm adversely affects the activity and selectivity of molybdenum trioxide/potassium oxide on alumina. However, treatment of this catalyst with hydrogen for several hours restored its activity.

Example 6:

This run utilized molybdenum trioxide and potassium oxide with saran carbon beads as a support. Tested were the ability of the catalyst to resist sulfur poisoning and its ability to regain high activity and selectivity by treatment with hydrogen. The catalyst was impregnated according to "Apparatus and Procedure". It was tested in the apparatus of Example 1. Levels of treatment were:

Weight percent MoO_3	11
Weight percent K_2O	4

Reaction conditions used were:

Temperature	400°C
Pressure	295 psia (20.8 kg/cm^2)
VHSV	300 hr^{-1}

Carbon monoxide conversions and product distributions at various times during the run are summarized below.

Time (Hours)	Carbon Monoxide Conversion (Mole Percent)	PRODUCT HYDROCARBON DISTRIBUTION (Mole Percent)					
		C_1	C_2	C_3	C_4	C_5	C_6
10	45	39.8	31.7	18.2	7.7	2.7	0
170	58	38.9	27.2	19.5	9.4	5.0	0
170.1	100 ppm carbonyl sulfide was added to the feed on a continuous basis.						
340	56	44.4	22.7	19.2	8.4	4.6	0.6
340.1	Carbonyl sulfide was eliminated from the feed. The feed was interrupted to treat the catalyst with hydrogen at 500°C for about sixteen hours.						
356	Feed restored.						
359	61	39.6	25.7	20.3	7.8	4.7	2.0

These data show that the activity and selectivity of the catalyst prior to exposure to carbonyl sulfide can be restored by treatment with hydrogen at 500°C for several hours.

Example 7:

Fischer-Tropsch catalysts consisting of molybdenum disulfide promoted with minor proportions of an alkaline material are known (U.S. Patent 2,490,488). However, these catalysts are taught to predominantly produce hydrocarbons of at least four carbon atoms and particularly hydrocarbons of at least five carbon atoms. To demonstrate the profound effect a support has upon the selectivity of such a catalyst, four different catalysts were prepared and then independently employed in a Fischer-Tropsch synthesis.

The first catalyst (Cat. #1) was only MoS_2 (98 plus percent purity).

The second catalyst (Cat. #2) was only MoS_2 deposited upon a coconut carbon support.

A third catalyst (Cat. #3) was prepared according to U.S. Patent 2,490,488. MoS_2 powder (12.06 g) was admixed with crushed KOH pellets (0.39 g) to yield a catalyst composition consisting of 96.9 weight percent MoS_2 and 3.1 weight percent KOH.

A fourth catalyst (Cat. #4) was prepared by impregnating coconut carbon with $(NH_4)_2MoS_3$ and K_2Co_3. The impregnating solution of $(NH_4)_2MoS_3$ and K_2Co_3 was prepared by combining $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (90.5 g) with K_2Co_3 (43.1 g), $(NH_4)_2S$ (503 g) and sufficient water to yield a 1000 ml solution. The catalyst composition analyzed as 11.5 weight percent MoO_3 and 4.8 weight percent K_2O.

(A) In the example of U.S. Patent 2,490,488, an unsupported catalyst consisting of 97-98 weight percent MoS_2 and 2-3 weight percent KOH converted a CO and H_2 mixture (of an unspecified mole or weight ratio) at 530°F (277°C), 200 psig (14.1 kg/cm^2) and an hourly space velocity (HSV) of 183 hr^{-1} to a product comprising, in weight percent carbon in hydrocarbon product:

Methane & Ethane	70
Propane	1.5
Butane	2.3
C_5+	27.5

The CO conversion was 69 percent.

U.S. Patent 2,490,488 does not report any results from a Fischer-Tropsch synthesis wherein a supported, alkaline-promoted MoS_2 catalyst was used.

(B) The third catalyst (96.9 weight percent MoS_2 and 3.1 weight percent KOH) was employed to convert a CO and H_2 mixture (H_2:CO volume ratio of 2.04:1) at 20.4 atm, 250°C and an HSV of 100 hr^{-1}. The apparatus described hereinbefore was employed. No conversion products were detectable by gas chromatography (GC). The GC had a sensitivity of about

0.03 weight percent. It was necessary to use temperatures in excess of 316°C (the maximum limit taught by U.S. Patent 2,490,488) to obtain a measurable conversion.

(C) Part (B) was repeated except that both Cat. #1 and Cat. #3 were independently used at the following conditions:

H_2:CO volume ratio	1.73:1
Pressure (atm)	19.4
Temperature (°C)	400
HSV (hr^{-1})	93

The results are reported below:

Catalyst Product Component	Cat.#1	Cat.#3
C_1 Hydrocarbons	63.8	50.5
C_2 Hydrocarbons	23.2	21.4
C_3 Hydrocarbons	6.6	7.1
C_4 Hydrocarbons	n.d.[1]	n.d.[1]
C_5+ Hydrocarbons	6.4	30.0

[1]Not detectable.

CO conversion was 10.6 percent with MoS_2 and 9.6 percent with Cat. #1.

(D) Part (B) was again repeated except that both Cat. #2 and Cat. #4 were independently used at the following conditions:

H_2:CO volume ratio	1.73:1
Pressure (atm)	19.4
Temperature (°C)	360
HSV (hr^{-1})	94

The results are reported below:

Catalyst Product Component	Cat.#2	Cat.#4
C_1 Hydrocarbons	74.7	49.7
C_2 Hydrocarbons	20.8	27.5
C_3 Hydrocarbons	7.2	18.2
C_4 Hydrocarbons	1.3	4.6
C_5+ Hydrocarbons	-	-

CO conversion was 67.3 percent with Cat. #2 and 60.7 percent with Cat. #4.

(E) Part (B) was again repeated except that Cat. #1, Cat. #3 and Cat. #4 were independently used at the following conditions:

H_2:CO volume ratio	0.75:1
Pressure (atm)	19.4
Temperature (°C)	400
HSV (hr^{-1})	162

Catalyst Product Component	Cat.#1	Cat.#3	Cat.#4
C_1 Hydrocarbons	48.8	32.8	42.8
C_2 Hydrocarbons	26.9	21.0	33.2
C_3 Hydrocarbons	10.5	13.4	19.5
C_4 Hydrocarbons	-	-	4.5
C_5+ Hydrocarbons	13.8	32.9	-

CO conversion was 6.5 percent with Cat. #1, 34.4 percent with Cat. #4, and 4.9 percent with Cat. #3.

These reported data (B-E) demonstrate not only the profound effect a support has upon the selectivity of a MoS_2 catalyst (promoted with alkali) but also its favorable effect upon its activity.

1. A process for producing saturated and unsaturated hydrocarbons containing two to four carbon atoms by contacting carbon monoxide and hydrogen at reactive conditions, characterized by contacting the carbon monoxide and hydrogen with a catalyst consisting of:

(A) between 1 percent and 95 percent by weight based upon the weight of the catalyst of at least one material selected from the group consisting of the metal, oxide or sulfide of molybdenum, tungsten, rhenium, ruthenium and platinum;

(B) between 0.05 percent and 50 percent by weight based upon the weight of the catalyst of at least one material selected from the group consisting of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium and thorium; and

(C) at least 1 percent by weight based upon the weight of the catalyst of a support.

2. The process of Claim 1 wherein C is carbon, alumina, silica, zirconia, magnesia, or mixtures thereof.

3. The process of Claim 1 wherein B is at least one material selected from the group consisting of the hydroxide, oxide or salt of lithium, sodium, potassium, rubidium and cesium.

4. The process of Claim 1 wherein A is at least one material selected from the group consisting of the sulfide, oxide or metal of molybdenum or tungsten.

5. The process of Claim 1 wherein C is present in a concentration of 50 to 80 percent by weight based upon the weight of the catalyst.

6. The process of Claim 5 wherein A is present in a concentration of from 10 to 50 percent by weight based upon the weight of the catalyst and B is present in a concentration of from 0.5 to 10 percent by weight based upon the weight of a catalyst.

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Application number

European Patent Office

EUROPEAN SEARCH REPORT

EP 79 100 988.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	DE - A1 - 2 457 417 (EXXON) * claims 1, 4, 5 * --	1,2
A	AT - B - 204 018 (ÖSTERREICHISCHE STICKSTOFFWERKE) * claims 1, 6 * --	1-4
A	GB - A - 762 704 (RHEINPREUSSEN) * claims 1, 8, 9 * --	1-3
A	GB - A - 1 205 677 (I.C.I.) * claims 1 to 3, 6 * --	2-4
A	GB - A - 1 397 293 (BRITISH PETROLEUM) * claim 1 * --	2
A	US - A - 4 141 817 (G.B. McVICKER et al.) * claims 1 to 8 * ----	2

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 07 C 1/04
B 01 J 23/58

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

B 01 J 23/58
C 07 C 1/04

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	29-11-1979	KNAACK

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