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PREPARATION OF REDUCED MAGNETITE SYNTHESIS CATALYST

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This invention relates to the synthesis of organic compounds. In one aspect this invention relates to the hydrogenation of a carbon oxide with an iron catalyst to produce organic compounds. In another aspect this invention relates to a method for manufacturing a hydrogenation catalyst which is useful in the production of organic compounds from carbon monoxide and hydrogen. Carbon oxides include carbon dioxide and organic compounds containing a carbonyl group, such as ketones, aldehydes, etc.

It has been known for some time that hydrogen and carbon monoxide may be made to react exothermically in the presence of catalysts under specific reaction conditions to form hydrocarbons and oxygenated compounds. In general, the synthesis of these organic compounds by the hydrogenation of carbon monoxide is accomplished in the presence of a metal or an oxide of a metal chosen from Group VIII of the periodic table as a catalyst at pressures below about 500 pounds per square inch gage and at temperatures below about 750° F.

The synthesis feed gas or reaction mixture comprises a mixture of about two mols of hydrogen per mol of carbon monoxide and may be prepared by the catalytic conversion of natural gas, steam, and carbon dioxide, or the partial oxidation of natural gas with oxygen.

Various techniques have been practiced to effect the reaction of hydrogen and carbon monoxide to produce organic compounds. Among these techniques are those known as fixed-bed catalyst operations and fluid-bed catalyst operations. The fixed-bed operation comprises passing a reaction mixture of hydrogen and carbon monoxide through a stationary bed of catalyst in a reaction zone, and the fluid-bed operation comprises passing a reaction mixture through a finely-divided catalyst mass suspended in the reaction mixture in the reaction zone.

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It is an object of this invention to provide a process for the synthesis of organic compounds.

Another object of this invention is to hydrogenate carbon monoxide in the presence of an iron catalyst to produce organic compounds having more than one carbon atom per molecule.

A further object is to provide a catalyst which is more selective and results in increased yields of hydrocarbons having more than one carbon atom per molecule and of oxygenated organic compounds.

It is another object of this invention to provide a method for manufacturing a hydrogenation catalyst.

It is still a further object of this invention to provide a novel catalyst for the hydrogenation of an oxide of carbon.

A still further object of this invention is to provide a method for manufacturing catalyst which is much less expensive than those heretofore used.

It is another object of this invention to provide an improved and relatively inexpensive hydrogenation catalyst.

Further objects and advantages of this invention will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention, a highly satisfac-

tory and improved catalyst for the hydrogenation of an oxide of carbon to produce organic compounds is manufactured from a naturally occurring iron compound, such as magnetite. According to an embodiment of this invention, naturally occurring magnetite is fused under conditions such that a molten mass is formed and thereafter the molten mass is cooled sufficiently to solidify the same. The solidified fused mass is reduced to produce a very active and selective catalyst containing iron as the major component.

Generally, the fusion of the naturally occurring magnetite is carried out at a temperature above about 2000° F.; the actual temperature will depend upon the other ingredients accompanying the magnetite, such as alumina, silica, and titanium oxide, which tend to lower the fusion temperature of the magnetite. After fusion and solidification, the fused mass is crushed and ground to a relatively small size, and then reduced with a reducing gas, such as hydrogen, at a temperature of at least 900° F. at atmospheric pressure and as high as 1600° F. The reduction may be carried out at substantially lower temperatures when super-atmospheric pressures are used; such temperatures may be as low as about 600° F. to about 800° F. The reduction process is carried out for a sufficient length of time to reduce about 90 to 95 per cent of the magnetite, usually indicated by the cessation of the formation of water.

A conveniently available and relatively cheap naturally occurring magnetite is Alan Wood ore which contains about 1 to 2 per cent alumina, about 1 per cent silica, about 0.4 to 1 per cent titanium oxide by weight, and the remainder magnetite (Fe_3O_4) and is a native ore of New Jersey. Since it is desirable in most instances to have present in the ultimate catalyst a minor amount of potassium oxide and other promoting ingredients, it is often necessary when using a naturally occurring magnetite to add these promoters to the catalyst. According to one modification of this invention, such promoters are incorporated into the catalyst by mixing them with the Alan Wood ore prior to fusion. The promoters are often added in the form of elements, oxides, carbonates, hydroxides, etc. to the Alan Wood ore and thoroughly mixed therewith before fusion. The promoters may be added and mixed dry or they may be added in the form of an aqueous solution and mixed with the Alan Wood ore to form a paste therewith. When the promoters are added as an aqueous solution to form a paste with the Alan Wood ore, the paste is dried, preferably at a temperature between about 200° F. and about 300° F. for several hours, and the resulting hard cake is crushed and then fused.

As used in this specification promoters or activators are used synonomously and include a material containing a metal or silicon incorporated in a minor amount with the iron compound during the catalyst preparation, or which is present as a minor component of the ultimate catalyst, and which has a substantially beneficial effect on the desired reaction. It is believed that, although promoters may be admixed with the magnetite during preparation of the catalyst in forms other than the oxides, the actual promoting materials in the ultimate catalyst usually, although not necessarily, consist of the oxides. Since naturally occurring magnetite often contains small amounts of alumina, silica, and titania, these promoting materials may be present in the final catalyst in small amounts regardless whether they were added or not. Usually alumina, silica, and titania of the original ore are present in reduced magnetite in a total amount less than about 2 weight per cent. Promoters or activators which may be added to the magnetite ore during the catalyst preparation comprise metals and silicon and their compounds including oxides, nitrates, sulfates, chlorides, carbonates, hydroxides, and organic compounds. For example, the following may be used singly or in combination: Co, Ni, Ti, Si, Al, TiO_2, CuO, Al_2O_3, SiO_2, K_2O, CoO, CeO_2, MgO, MnO, ThO_2, MoO_3, K_2CO_3, $Al(COOH)_3$, $Al(NO)_3$, $Mn(NO_3)_2$, ZnO, $Ce(OH)_4$, KOH, $Co(NO_3)_2$, H_2MoO_4, KCl, $SiCl_4$, $AlCl_3$, H_2SiO_3, Rb_2CO_3, and Cs_2CO_3. When present in the final catalyst preparation as promoters, the oxides of silicon, aluminum, titanium, molybdenum, cobalt, copper, manganese, and thorium preferably constitute in total between about 0.1 and about 10 weight per cent of the catalyst. Potassium calculated as the oxide has been found to be a very desirable promoter or activator when present in the resulting catalyst between about 0.2 and about 2.5 per cent.

When the promoters are added to the Alan Wood ore and fused, it is believed that they often form a solution with the Fe_3O_4 in the molten state and, when cooled and solidified, may be present as a solid solution with Fe_3O_4. Thus, it is preferred that such promoters be added prior to fusion. During fusion certain additive materials decompose and remain in solid solution, for example, as the oxides. The reduction process reduces Fe_3O_4 to metallic iron (Fe) and may in some instances reduce the promoters.

The exact composition of the resulting catalyst with respect to promoters is not certain, but the promoters are considered to be present in minor amount in the ultimate catalyst composition as the oxides unless added in a form that does not change during fusion. Whatever the exact form of the promoters in the reduced catalyst, they are found to have a great influence upon the activity and selectivity of the catalyst itself, especially when incorporated in the catalyst according to this invention.

Since iron in the reduced form is somewhat malleable, it is highly desirable to crush and grind the material to the required size for use as catalyst prior to reduction. Where the catalyst is to be used in a fluidized operation in a finely divided form, the fused material is ground to a size less than about 30 mesh, and formed, e. g. by pelletting, briquetting, extrusion, etc., prior to reduction and then reduced. After reduction the material is broken into its previously finely divided state but with much less effort than would be required had the reduced material not been ground and pulverized prior to reduction.

Merely fusing Alan Wood ore and reducing the solidified fused material often produces a sufficiently active catalyst for the hydrogenation of carbon monoxide since the ore itself contains small amounts of alumina, silica, and titania. However, when it is desired to produce the minimum amount of methane and carbon dioxide in the hydrogenation of carbon monoxide, a minor proportion of a material containing an alkali metal, such as potassium, or an alkaline earth, should be present in the catalyst. The presence of potassium in the ultimate catalyst composition is achieved by incorporating potassium carbonate, potassium hydroxide, or potassium nitrate with

the Alan Wood ore prior to fusion or, as is preferable in some instances, with the fused material just prior to reduction. In the latter case the carbonate, hydroxide, or nitrate of potassium is added after the ore has been fused. Generally, it is desirable to have an increased amount of alumina, silica, or titania present in the ultimate catalyst than is present in the Alan Wood ore itself and, consequently, one or more of these materials are added in minor amount in the form of the compounds previously mentioned to the Alan Wood ore prior to fusion. It is understood that other promoters may be added in addition or instead of these mentioned above without departing from the scope of this invention.

Reducing naturally occurring magnetite without fusion will produce a hydrogenating catalyst. However, to obtain both maximum activity and selectivity it is much preferred to fuse the naturally occurring magnetite prior to reduction, especially when it is necessary to add additional promoters to the catalyst; since by fusion the promoters are usually brought into solution with the magnetite. Even in the case of naturally occurring magnetite, such as Alan Wood ore, only a portion of the alumina and silica in the ore may be present in solid solution with the magnetite. To obtain more of this material in solid solution, the ore is fused in order that the beneficial effect of all of the alumina, silica, and titanium oxide present in the original ore may be realized.

In a modification of this invention, the naturally occurring magnetite is not fused but is only heated to a moderately high temperature, preferably above 1000° F. This moderate temperature treatment is referred to herein as calcination and may be effected in an oxidizing, reducing, or inert atmosphere without departing from the scope of this invention. In most instances the calcination is carried out in a substantially inert or a substantially oxidizing atmosphere. In this moderate temperature heat treatment, a lower temperature is used than in the case of fusion and for this reason replacing fusion by such a calcination treatment results in a much cheaper and more economical process for the manufacture of a synthesis catalyst. The promoting materials may be added either prior or subsequent to the calcination treatment. In case of the alkali metal and alkaline earth metals, such promoters are preferably added subsequent to calcination. Other promoters if used in addition to the alkali promoters are preferably added prior to calcination. After the naturally occurring magnetite, such as Alan Wood ore, has been calcined, with or without the presence of added promoting material, the calcined material is ground to the desired size and then reduced. The calcination of the ore may be carried out at a temperature as low as 1000° F. but is usually carried out at a temperature between about 1400 and about 1600° F. for a time between about 2 and about 12 hours, which time depends, of course, upon the temperature used. At higher temperatures shorter heating periods are necessary than at lower temperatures. As previously mentioned, it is preferred to add the potassium carbonate or hydroxide after calcination either by mixing dry or by mixing an aqueous solution of the compound with the calcined material. When the promoter is mixed as an aqueous solution with the calcined material to form a paste, the paste is dried, preferably at a temperature between 200° F. and 300° F. for at least two hours. After the calcined material has been dried, it is reduced at a temperature preferably between about 1400° F. and about 1500° F., or at lower or higher temperatures as previously discussed.

Coking inhibitors may be added to the fused or calcined mass just prior to reduction. Such coking inhibitors include $SnCl_4$, and $Pb(NO_3)_2$.

Calcining the naturally occurring magnetite in the presence of added promoters may have much the same effect as the fusion since it may cause a dispersion of the promoters on the surface of the particles of the naturally occurring magnetite, thus increasing the beneficial effect of the promoting materials.

The catalyst of this invention may be employed either in stationary bed or in fluidized operations with improved results; however, it is much preferred to use the catalyst in the fluidized operation.

A preferred embodiment of this invention involves flowing a gaseous mixture comprising hydrogen and a carbon oxide to be hydrogenated upwardly in a reaction zone in contact with a mass of finely divided metallic iron catalyst prepared in the manner described herein. The hydrogen and carbon oxide reactants are passed as gases through the reaction zone, under conditions effective to react all, or a major proportion, of the carbon oxide reactant. The gaseous mixture is passed upwardly through the mass of catalyst at a velocity sufficient to suspend or entrain the catalyst mass in the gas stream. Preferably, the velocity of the gas stream passing through the reaction zone is sufficiently low to maintain the catalyst mass in a dense, fluidized, pseudo-liquid condition. However, the velocity may be sufficiently high to entrain at least a substantial portion of the finely-divided catalyst in the gas stream to form a continuous catalyst phase which circulates with the flowing gas stream, without departing from the scope of this invention. In the former condition the catalyst mass may be said to be suspended in the gas stream, but not entrained therein in the sense that there is movement of the catalyst mass as such in the direction of flow of the gas stream. When operating in the pseudo-liquid condition it is preferred to maintain the upward velocity of the gas stream sufficiently high to maintain the fluidized catalyst mass in a highly turbulent condition in which the catalyst particles circulate at a high rate in the pseudo-liquid mass. In this pseudo-liquid condition of operation a small proportion of catalyst in the fluidized mass may become entrained in the gas stream emerging from the upper surface of the fluidized mass whereby catalyst thus entrained is carried away from the mass.

In the present process it is preferred to employ the hydrogen and carbon oxide in ratios such that there is a substantial excess of hydrogen. Therefore, the charging rate in the present process is defined by reference to the rate at which the carbon oxide is charged, in terms of standard cubic feet, in the gas form, of the carbon oxide per hour per pound of the metal catalyst in the dense pseudo-liquid mass of catalyst in the reaction zone. The fluidized process is preferably operated at a minimum space velocity equivalent to charging rate of about 1.0 standard cubic foot of the carbon oxide reactant, per hour per pound of the metal catalyst in the dense catalyst phase. A standard cubic foot of the carbon oxide is that quantity of a normally gaseous carbon oxide which would occupy one cubic foot of atmospheric pressure at 60° F., or an equiva-

lent quantity of a normally liquid carbon oxide reactant.

The catalyst material employed in the present invention is a finely divided powder comprising metallic iron containing the appropriate amount of promoter or promoters incorporated with the iron in the manner described hereinbefore, or a mixture of such iron catalyst and other catalytic materials or non catalytic materials. While the catalyst powder consists essentially of such catalytic material prepared according to this invention, it may include also ingredients, and supporting materials, such as alumina, silica gel, bentonite type clay, etc. In this specification and claims the catalyst composition is described by reference to its chemical condition prior to contact with the reactants.

Preferably, the powdered catalyst initially contains no more than a minor proportion by weight of material whose particle size is greater than 250 microns. Preferably, also, the greater proportion of the catalyst mass comprises material whose particle size is smaller than 100 microns, including at least 25 weight per cent of the material in particle sizes smaller than 40 microns. A highly desirable powdered catalyst comprises at least 75 per cent by weight of material smaller than 150 microns in particle size, and at least 25 per cent by weight smaller than about 40 microns in particle size.

In the preferred form of the invention with the catalyst present in a pseudo-liquid condition, the powdered catalyst mass of iron is maintained in a reactor substantially larger than the volume occupied by the catalyst mass in the fluidized condition. In this operation all but a minor proportion of the catalyst mass is contained in the dense fluidized pseudo-liquid mass, which may be designated as the dense phase of the catalyst. The dense phase of the catalyst occupies the lower part of the reactor while that part of the reactor above the dense phase is occupied by a mixture of gases and powdered catalyst in which the concentration of catalyst is much lower, and of a different order of magnitude, than the concentration of the catalyst in the dense phase. This diffuse phase may be said to be a disengaging zone in which the solids lifted above the dense phase by the gas stream are disengaged therefrom and returned to the dense phase to the extent that such solids are present in the diffuse phase in excess of the carrying capacity of the gas stream at the superficial velocity of the gas stream. The latter is the velocity at which the gas stream would flow through the reactor in the absence of catalyst. In the dense phase the concentration of the catalyst in the gas stream varies from a maximum near the gas inlet to a minimum in the upper part of this phase. Likewise the concentration of catalyst in the diffuse phase varies from a maximum near the upper surface of the dense phase to a minimum in the upper part of the reactor. Between the dense phase of high average concentration and the diffuse phase of very much lower average concentration, there is a relatively narrow zone in which the concentration of solids in the gas stream changes in a short space from the high concentration of the dense phase to the low concentration of the diffuse phase. This zone has the appearance of an interface between two visually distinct phases.

This dense phase operation ordinarily involves employment of catalyst powders and gas velocities such that a relatively small portion of the fluidized catalyst is carried away by entrainment, and it is necessary, therefore, to provide means in the reactor for separating such entrained catalyst and returning it to the dense phase, or to provide means externally of the reactor to separate the small amount of entrained catalyst from the gas stream and return it to the reactor, or otherwise to recover catalyst from the product gas stream.

When catalyst is permitted to pass out of the reactor by entrainment in the gas stream in either the pseudo-liquid operation or the continuous phase operation, it is necessary to return such catalyst to the reactor, or replace it with fresh or revivified catalyst, in order to maintain the desired volume of fluidized catalyst in the reaction zone.

The pseudo-liquid operation in which the finely powdered catalyst is employed in a form consisting of the metallic iron catalyst and containing at most minor proportions of promoting agents provides very high catalyst concentrations in the reaction zone. The employment of the finely powdered metal catalyst in a fluidized bed with efficient cooling means also is a factor in permitting the use of high catalyst concentrations, since it facilitates the removal of heat from the relatively concentrated reaction zone. The pseudo-liquid operation, employing the finely divided metal catalyst, results in initial catalyst concentrations of at least 30 pounds per cubic foot of the fluidized dense catalyst phase, while preferred gas velocities result in initial concentrations of 40 to 120, or more, pounds per cubic foot of dense phase. It will be understood that these figures refer to the initial average concentration in the dense phase. The accumulation of reaction products on the catalyst particles as the operation proceeds reduces the catalyst density and increases the bulk of the dense fluidized mass.

With the improved iron catalyst of this invention temperatures in the range of about 350° F. to about 750° F. and pressures between atmospheric pressure and the maximum pressure at which condensation is avoided may be employed. It is desirable, however, to employ pressures of at least 80 p. s. i. and preferably about 150 to about 500 p. s. i.

In this specification, pressures are expressed as pounds per square inch gage and gas volumes as cubic feet measured at 32° F. and atmospheric pressure.

The linear velocity of the gas stream passing upwardly through the dense phase is conveniently expressed in terms of the superficial velocity, which is the linear velocity the charge gas stream would assume if passed through the reactor in the absence of catalyst, and takes into account the shrinkage in volume caused by the reaction. These superficial velocities preferably are in the range of from 0.1 to 6 feet per second for the dense phase operation. When operating with a continuous catalyst phase in which the catalyst is entrained in the flowing gaseous mixture, velocities as high as 40 feet per second may be employed.

The reactants are passed into and through the reaction zone at a space velocity equivalent to at least 1.0 standard cubic foot of the carbon oxide per hour per pound of metal catalyst in the dense catalyst phase. In the hydrogenation of carbon monoxide with the iron catalyst of this invention, it is preferred to operate at a space velocity equivalent to at least 2.0 standard cubic feet of carbon

monoxide per hour per pound of iron catalyst in the dense catalyst phase. The charging rate is defined by reference to the carbon monoxide reactant, since the ratio of the hydrogen reactant to the carbon monoxide reactant in the charge gas may vary within wide limits. This ratio of hydrogen to carbon monoxide is usually in excess of 1:1, and preferably at least 2:1, and may be as high as 10:1. At the 1:1 ratio the preferred charging rate of hydrogen and carbon monoxide would, therefore, be at least 4.0 standard cubic feet per hour per pound of iron catalyst in the dense catalyst phase. At the 2:1 ratio this preferred rate would be 6.0 standard cubic feet of hydrogen and carbon monoxide.

According to a preferred modification of this invention, a fresh feed gas having an H_2:CO ratio higher than the ratio in which these compounds are converted to other compounds is employed and the mol ratio of hydrogen to carbon monoxide in the charge to the reactor is increased to the desired figure by recycling a portion of the unconverted gas, after removal of part or all of the product liquid. Preferably, a gas containing excess hydrogen is processed under conditions effective to react all, or a major proportion, of the carbon monoxide, and a portion of the product mixture, after removal of the greater part of the normally liquid product, is recycled in volumetric ratios to the fresh feed gas of 0.5:1 to 10:1.

Fluid operations are carried out at temperature levels which are relatively high as compared to those which would be permissible in fixed or stationary catalyst bed operations under comparable operating conditions. This results from the excellent heat transfer capacity of the fluidized mass of finely divided iron and the effect of excess hydrogen in minimizing carbon formation.

The following examples are illustrative of the procedure for manufacturing a hydrogenation catalyst according to this invention and show the final catalyst composition and the yield of hydrocarbon oils and oxygenated compounds produced by the hydrogenation of carbon monoxide. Since the examples are illustrative only of the application and composition of the catalyst, they should not be considered to be unnecessarily limiting to the present invention and are offered merely as a better understanding of the process for the manufacture of a novel catalyst and its performance.

The results obtained when using the catalysts prepared according to this invention are presented in conventional tabular form. The contraction, yield of observed oil and water may be taken as indications of catalyst activity. The yield of observed oil represents the product collected in the primary receiver at room temperature and operating pressure and in the secondary receiver at about −30° F. and atmospheric pressure. This yield of oil is not the total yield of organic compounds since it does not include most of the gaseous hydrocarbons made or the organic compounds soluble in the water product. The yield of observed water represents the aqueous layer recovered in the primary and secondary receiver and includes the organic compounds soluble therein.

The inspections on the oil and water were obtained by conventional methods of analysis and these data may be used as a measure of catalyst selectivity. The unsaturate content of the oil is calculated and reported as the "mol per cent monoolefins" although there may be some diolefins present. The "weight per cent water-KFR" is obtained by use of the Karl Fischer Reagent (KFR) and the difference between that value and 100 per cent is a measure of the organic chemicals (oxychemicals) contained in the observed water product. All of the oxygenated organic compounds (acids, alcohols, aldehydes, ketones, etc.) are not present in the observed water but some are present also in the observed oil product. The yield of acids contained in the water is expressed as the equivalent yield of acetic acid although higher molecular weight acids are also present.

EXAMPLE I

Powdered Alan Wood ore in an amount of about 13,600 grams was thoroughly mixed in a ball-mill with 98 grams of TiO_2 and 216 grams of K_2CO_3 and the resulting mixture was ground to about 20 to 30 mesh in size. The mixed and ground material was then fused in a fusion apparatus at a temperature of about 2600° F. until the material became a molten mass. The fusion equipment comprised a water cooled copper mold fitted with a carbon electrode. The material was fused in an electric arc projected from the carbon electrode to the base plate of the copper mold. The initial arc was started with the aid of a small quantity of steel shot placed in the bottom of the mold. When the steel shot proceeded to melt, the ore mixture was added slowly. The fusion apparatus drew approximately 600 amperes while the voltage was held constant at 40 volts. The voltage was maintained constant by the automatic regulation of the carbon electrode above the melt. The resulting liquid mass was removed from the fusion apparatus and cooled until it solidified. The solidified mass was broken into large chunks and crushed in a jaw crusher. The material was very brittle and easily crushed. The fragments of molten material were then charged to a reduction chamber in which the material was reduced in the presence of hydrogen at a temperature between about 1400 and 1480° F. for a period of about six hours. A maximum reduction temperature of 1480° F. was observed during the reduction. The average temperature was maintained for two hours after the formation of water ceased.

The reduction process was carried out by passing a stream of hydrogen upwardly through the reduction chamber in which the fragments formed a stationary bed. The catalyst thus produced was designated No. 410–1. This No. 410–1 catalyst contained by weight approximately 1 part TiO_2, 1.5 parts K_2O, 0.5 part SiO_2, and 100 parts metallic iron (not including silica, alumina, and titania originally present in the Alan Wood ore).

The catalyst produced in the above manner was then tested for the hydrogenation of carbon monoxide to produce hydrocarbons having more than one carbon atom per molecule and oxygenated organic compounds by contacting the catalyst with a gaseous stream comprising hydrogen and carbon monoxide in a mol ratio between about 1.5:1 and about 1.6:1. The carbon dioxide in this gaseous stream averaged about 4.3 volume per cent and light hydrocarbons and nitrogen averaged about 1.7 volume per cent. The reaction conditions and the results obtained from the

hydrogenation of carbon monoxide with the fused iron catalyst are shown in Table I below.

Table I

Total Hours of Operation	44	92	116	140	164	188	212	260
Pressure, p. s. i.	250							
Catalyst Temp., Degrees F	500	520	540	560	580	600	620	630
Gas Rate, V./Hr./V	168	182	190	192	222	240	237	256
Contraction, Per Cent	38	48	49	56	56	60	60	65
Obs. Oil, cc./m.³ (Total gas at 32 degrees F.)	20	48	67	74	76	75	80	81
Obs. H_2O, cc./m.³ (Total gas at 32 degrees F.)	20	28	32	45	55	68	85	82
Prim. Oil, cc./m.³	15	40	44	49	52	53	59	54
Per Cent CO converted	----	----	----	----	93	----	----	----
Per Cent CO → CO_2	----	----	----	----	22	----	----	----
Feed Gas, Volume Per Cent:								
CO_2	3.7				4.8			
H_2	58.2				55.3			
CO	37.5				37.2			
Residual	0.6				2.7			
H_2/CO	1.6:1.0				1.5:1.0			
Mol Weight	14				14			
Product Gas, Volume Per Cent:								
CO_2	----				28.9			
H_2	----				53.2			
N_2	----				----			
CO	----				5.6			
CH_4	----				10.7			
C_2	----				1.6			
Mol. Weight	----				18			
Oil Inspections Distillation:								
I. B. P., Degrees F	----				133			
5%	----				150			
10%	----				158			
50%	----				333			
90%	----				682			
E. P.	----				701			
Mol. Weight	130				143			
Monoolefins, mol Per Cent	35				57			
Wax, Weight Per Cent	7				7			
Wax, M. P., Degrees F	185				166			
H_2O Inspections:								
H_2O, K. F. R., Weight Per Cent	82				84			
Per Cent Acid, Weight Per Cent CH_3COOH	5.1				2.4			

Table II below shows the composition of the catalyst with respect to wax and carbon after approximately 250 hours of operation at about 630° F.

Table II

Catalyst No.	Oil and Wax, Weight Per Cent	Wax, M. P. °F.	Carbon, Weight Per Cent
410-1	6.4	234	4.3

Table III below is a summary of the composition and yields of various catalysts prepared in the manner of Example I. Promoters were incorporated in the catalyst prior to fusion, then the ore was fused and subsequently reduced. The compositions of the catalysts are reported in parts by weight and do not include amounts of alumina, silica, and titania present in the original Alan Wood ore.

Table III

Cat. No.	Original Mixture, Grams					Catalyst Composition, Parts by weight, Iron = 100			
	Alan Wood Ore	K_2CO_3	Al_2O_3	CuO	TiO_2	K_2O	CuO	Al_2O_3	TiO_2
375-3	13,600	286	295	----	----	2.0	----	3.0	----
396-1	13,600	433	491	----	----	3.0	----	5.0	----
406-1	6,800	50	----	98	----	0.7	2.0	----	----
407-1	6,800	108	----	245	----	1.5	5.0	----	----
408-1	6,800	108	147	244	----	1.5	3.0	3.0	----
409-1	13,600	216	98	----	----	1.5	----	1.0	----
411-1	13,600	216	----	----	128 H_2SiO_3	1.5	----	----	1.0 SiO_2
416-1	6,800	108	----	----	147	1.5	----	----	3.0
417-1	6,800	108	----	----	245	1.5	----	----	5.0
418-1	6,800	108	49	----	147	1.5	1.0	----	3.0
419-1	6,800	108	490	----	----	1.5	10.0	----	----
420-1	6,800	108	----	----	----	1.5	----	----	----
421-1	6,800	108	----	----	----	1.5	----	----	5.0 MgO
422-1	6,800	108	----	----	----	1.5	----	----	5.0 ZnO
425-1	3,050	49	----	----	----	1.5	----	----	5.0 CeO_2
426-1	6,800	108	147	490	----	1.5	10.0	3.0	----
427-1	6,800	108	----	245	147	1.5	5.0	----	3.0
428-1	6,800	216	147	245	----	3.0	5.0	3.0	----
430-1-2	3,490	110	1,005	----	----	3.0	----	40.0	----
431-1	3,410	100	1,350	----	----	3.0	----	60.0	----
432-1-2	2,853	90	1,640	----	----	3.0	----	80.0	----
433-1	3,910	124	563	----	----	3.0	----	20.0	----
434-1	2,850	90	2,050	----	----	3.0	----	100.0	----
435-1	6,800	216	----	----	----	3.0	----	----	----
436-1	6,800	108	----	----	245 Co	1.5	----	----	5.0 Co
439-1	6,800	108	----	----	245 Ti	1.5	----	----	5.0 Ti
440-1	6,800	108	----	----	245 Si	1.5	----	----	5.0 Si

Table III—Continued

Cat. No.	Synthesis Conditions and Results, 250 p. s. i. pressure							Catalyst Composition After Use		
	Reduction Temp., F.	Gas Rate, V./Hr./V.	Temp., F.	Obs. Oil, cc./m³	Water, cc./m³	Per Cent CO→CO₂	Per Cent Conv.	Oil, Wt. Per Cent	Carbon, Wt. Per Cent	Hours in Use
375-3	1,500	189	580	123	98	30	97	7.0	3.0	210
396-1	1,485	171	580	134	110	29	97	7.3	3.8	210
406-1	1,460	236	635	81	93	32	97	4.1	5.4	210
407-1	1,460	252	600	95	66	32	97	4.3	3.4	300
408-1	1,460	200	600	113	91	30	97	2.4	2.9	300
409-1	1,460	160	620	109	87	52	88	5.2	3.5	300
411-1	1,480	235	620	91	79	25	95	4.7	4.4	300
416-1	1,505	214	600	87	91	36	98	4.0	4.4	260
417-1	1,505	251	620	106	89	33	98	3.8	4.7	290
418-1	1,505	208	600	103	88	30	97	2.9	2.7	240
419-1	1,505	245	630	111	89	32	96	2.7	1.8	240
420-1	1,505	240	600	97	87			6.2	5.8	260
421-1	1,505	172	560	90	68	32	95	6.1	5.9	215
422-1	1,450	235	580	114	84	38	97	4.7	4.2	150
425-1	1,450	244	600	105	88	28	98	6.4	4.6	190
426-1	1,450	245	600	155	77	24	97	1.3	5.0	190
427-1	1,450	184	580	149	80	28	97	3.8	2.9	240
428-1	1,450	233	580	111	78	27	97	4.0	3.6	240
430-1-2	1,455	200	650	100	89	27	97	2.0	2.0	240
431-1	1,455	200	650	94	91	26	96	2.1	2.0	290
432-1-2	1,455	195	650	93	72	32	95	2.5	1.0	290
433-1	1,455	220	635	100	93	32	97	2.3	2.3	290
434-1	1,460	137	660	99	93	26	92	1.8	1.2	290
435-1	1,460	243	660	91	88	24	97	4.4	6.6	340
436-1	1,450	158	580	103	71	27	97	6.3	3.9	340
439-1	1,450	207	620	96	82	44	95	3.7	2.6	210
440-1	1,450	150	560	58	43	32	88	5.5	1.9	210

EXAMPLE II

Approximately 274 grams of KOH was dissolved in 1600 cc. of distilled water and this solution was mixed with about 13,600 grams of powdered Alan Wood ore in a mechanical mixer. After the ore was thoroughly wetted by the solution and became a pasty mass, 69 grams of titanium oxide and 392 grams of aluminum oxide were added and the mixture was stirred until uniform. The mixture was then allowed to dry overnight in porcelain dishes at a temperature of about 220° F. To facilitate fusing, the hard dry cake was ground to about 20 mesh. The resulting mixture was then fused in the manner described in Example I, after which the material was reground to the extent that about 30 per cent passed through a 200 mesh screen. The ground material was then pelleted to about ⅛ inch in diameter and reduced at a temperature of about 1400° F. in the manner described in Example I. After reduction the catalyst composition was approximately as follows: 4 parts Al_2O_3, 1 part TiO_2, 0.5 part SiO_2, 2.4 parts K_2O, and 100 parts iron. This catalyst was designated as catalyst No. 415–1. As in Example I, catalyst No. 415–1 was used to hydrogenate carbon monoxide to produce hydrocarbons having more than one carbon atom per molecule and oxygenated organic compounds. Table IV below shows the operating conditions and results obtained when using the catalyst composition prepared as in Example II. Table V shows the composition of the catalyst after use for about 300 hours.

Table IV

Total Hours of Operation	40	64	88	112	208	232	280	304
Pressure, p. s. i.	250							
Catalyst Temp., °F.	500	520	540	560	585	600	620	625
Gas Rate, V./Hr./V.	165	145	175	194	174	218	185	202
Contraction, Per Cent	40	46	34	46	58	60	61	60
Obs. Oil, cc./m.³ (Total Gas at 32 °F.)	21	60	54	109	151	111	130	104
Obs. H_2O, cc./m.³ (Total Gas at 32 Deg. F.)	23	39	37	21	58	79	86	80
Prim. Oil, cc./m.³	14	49	39	86	116	86	91	72
Per Cent CO converted	-----	-----	-----	95	-----	-----	98	----
Per Cent CO→CO_2	-----	-----	-----	37	-----	-----	35	----
Feed Gas, Vol. Per Cent:								
CO_2			3.5		4.2		1.4	
H_2			53.0		55.6		56.8	
CO			39.8		40.2		38.6	
Residual			3.7		-----		3.2	
H_2/CO			1.4:1.0		1.4:1.0		1.5:1.0	
Mol. Weight			14		14		13	
Product Gas, Vol. Per Cent:								
CO_2				31.3	-----		38.7	
H_2				41.6	-----		37.6	
N_2				1.4	-----		-----	
CO				2.5	-----		2.2	
CH_4				18.9	-----		19.2	
C_2+				4.3	-----		2.3	
Mol. Weight				22	-----		23	

Table IV—Continued

Total Hours of Operation	40	64	88	112	208	232	280	304
Pressure, p. s. i.	250							
Oil Inspections, Distillation:								
I. B. P., °F.					129			
5%					160			
10%					167			
50%					244			
90%								
EP, °F.					608			
Mol. Weight	130				120			
Monoolefins, Mol. Per Cent	27				46			
Wax, Weight Per Cent	10				7			
Wax, M. P., °F.	207				216			
H_2O Inspections:								
H_2O, Weight Per Cent K. F. R.					91			
Per Cent Acids (Wt. Per Cent CH_3COOH)	2.5				1.8			

Table V

Catalyst No.	Oil and Wax, Wt. Per Cent	Wax, M. P., °F.	Carbon, Wt. Per Cent
415-1	5.1	238	3.1

Table VI shows the results obtained by the hydrogenation of carbon monoxide with similar catalysts prepared in the manner of Example II having various compositions. Small amounts of titania, alumina, and silica present in the original ore have not been reported in the analysis of the catalyst. The total amount of these compounds present in the original ore is usually less than about two or three per cent by weight of the final catalyst composition.

Table VI

Cat. No.	Original Mixture, Grams					Catalyst Composition, Parts by weight—Iron=100			
	Alan Wood Ore	KOH	TiO_2	Al_2O_3	H_2SiO_3	K_2O	TOi_2	Al_2O_3	SiO_2
412-1	13,600	274	69			2.4	1.1	1.0	0.8
413-1	13,600	175	69			1.5	1.1	1.0	0.8
413-2	13,600	175	69			1.5	1.0	1.0	1.0
414-1	13,600	175	69	392		1.5	1.0	4.0	0.5
436-1	6,800	88			192	1.5			3.0
437-1	6,800	88			320	1.5			5.0

Cat. No.	Synthesis Conditions and Results, 250 p. s. i. pressure							Catalyst Composition		
	Reduction Temp., F.	Gas Rate, V./Hr./V.	Temp., F.	Obs. Oil, cc./m.³	Water, cc./m.³	Per Cent $CO \rightarrow CO_2$	Per Cent Conv.	Oil, Weight Per Cent	Carbon, Weight Per Cent	Hours in Use
412-1	1,500	232	620	96	51	30	95	5.1	5.0	260
413-1	1,500	260	600	82	40	25	95	10.7	4.2	260
413-2	1,525	235	640	106	44	28	98	3.3	1.7	260
414-1	1,480	228	540	115	47	35	96	5.0	2.4	280
436-1	1,460	177	650	55	54	31	86	1.8	2.2	340
437-1	1,460	208	650	84	78	28	95	2.4	1.9	340

EXAMPLE III

Approximately 9080 grams of powdered Alan Wood ore were mixed thoroughly with approximately 194 grams of powdered Al_2O_3 and fused by the electric arc method described in Example I. The melt was removed from the fusion apparatus and cooled to form a solid mass. The solid mass was crushed in a jaw crusher and milled in a disc mill to about 30 mesh in size. Approximately 2.7 grams of K_2CO_3 (CP) were dissolved in 25 cc. of distilled water. This solution was added to 500 grams of the fused powder and subsequently an additional 80 cc. of distilled water was added during stirring. The resulting paste was dried in porcelain dishes at about 200° F. for about 12 hours. The dried cake was crushed and pulverized and subsequently pelleted to ⅛ inch diameter pellets. The pelleted material was then reduced with hydrogen at a temperature of about 1475° F. until the formation of water ceased and thereafter at 1450° F. for one hour. This catalyst had a composition by weight of about 3 parts Al_2O_3, about 0.5 part K_2O, a small amount silica and titania present from the original ore, and 100 parts metallic iron. The catalyst was designated No. 373-2.

The reduced catalyst prepared in the above manner was charged to a reaction zone taking precautions to maintain the catalyst in an inert atmosphere, such as carbon dioxide, during charging. A stream of hydrogen was passed through the reaction chamber while the chamber was brought to the desired process temperature. After the catalyst and reaction chamber were at the desired temperature, a stream of hydrogen and carbon monoxide at a mol ratio of about 1.4:1 was passed through the catalyst mass. This was continued for about 260 hours after which the ratio of hydrogen to carbon monoxide was changed to about 1.7:1 and continued at this mol ratio for about 75 hours. The temperature during operation was gradually increased from about 500° F. to about 620° F. The operating conditions and results obtained with this catalyst are shown in Table VII below. The analysis of the used catalyst is summarized in Table VIII below.

Table VII

Total Hours of Operation	64	88	160	184	209	257	329
Pressure, p. s. i.	250						
Catalyst Temp., °F.	520	540	560	580		600	620
Gas Rate, V./Hr./V.	138	174	153	121	205	167	142
Contraction	42	48	42	47	44	44	38
Obs. Oil, cc./m.³ (Tot. Gas at 32 °F.)	76	60	64	60	47	38	14
Obs. H_2O, cc./m.³ (Tot. Gas at 32 °F.)	59	68	83	73	69	71	68
Prim. Oil, cc./m.³	60	64	54	38	24	22	0
CO converted				97			
$CO \rightarrow CO_2$				34			
Feed Gas, Vol. Per Cent:							
CO_2	5.7			2.3		3.5	2.3
H_2	53.3			54.1		54.0	56.3
CO	34.7			38.7		39.1	32.6
Residual	6.3			4.9		3.4	8.8
Mol. Weight				15		15	18
H_2/CO	1.5:1.0			1.4:1.0		1.4:1.0	1.7:1.0
Product Gas, Vol. Per Cent:							
CO_2				29.5			
Co				2.3			
Unsaturates				3.1			
Mol. Weight	20	22	21	24	23	23	21
Oil Inspections, Distillation:							
I. B. P., °F.				96			
5%				116			
10				132			
50				274			
90				(580)			
E. P.				638			
Mol. Weight				121			
Monoolefins, mol. per cent				48			
Wax, Weight Per Cent				1			
M. P., Wax, °F.				146			
H_2O Inspections:							
H_2O, K. F. R., Weight Per Cent				87			
Per Cent Acid (Weight Per Cent CH_3COOH)				0.8			

Table VIII

Catalyst No.	Oil and Wax, Weight Per Cent	Wax, M. P., °F.	Carbon Weight, Per Cent
373-2	0.7	215	2.1

EXAMPLE IV

Approximately 14.2 grams of H_2MoO_4 (85 per cent acid) was dissolved in a solution of 80 cc's of water and 20 cc's of NH_4OH (28 per cent NH_3). The basic molybdate solution was thoroughly impregnated into 500 grams of powdered Alan Wood ore by mixing thoroughly until the formation of a paste. The paste was dried overnight at a temperature of about 220 to about 230° F. The dried material was then crushed to a powder and calcined at a temperature of about 1450° F. for about two hours in a muffle furnace After calcination the material was admixed with about 7.9 grams of K_2CO_3 dissolved in 100 cc. of water. The resulting pasty mixture was allowed to dry at about 220° F. for several hours and then ground to a size less than about 30 mesh in preparation for pelleting. The calcined material after impregnation with K_2CO_3 was pulverized and pelleted to about ⅛ inch diameter pellets. The pelleted material was then reduced with hydrogen at a temperature of about 1490° F. for several hours until the formation of water ceased and was continued thereafter for about one hour at about 1450° F. The resulting catalyst was

designated No. 395–1 and had a composition approximately as follows: 3 parts by weight MoO_3, 1.5 parts by weight K_2O, very small amounts of alumina and silica present in the original ore, and 100 parts by weight metallic iron. This catalyst was charged to a reaction zone in an inert atmosphere until the temperature of reaction had been reached. When a temperature of about 500° F. had been reached, a stream of hydrogen and carbon monoxide in a mol ratio of about 1.9:1 was passed through the catalyst. This was continued for a sufficient length of time to obtain operating data. Operation conditions and results for this particular catalyst are shown in Table IX below.

Table IX

Total Hours of Operation	38	61	133	167	191	215
Pressure, p. s. i.	250					
Catalyst Temp., °F.	500	520	560	580	600	620
Gas Rate, V./Hr./V.	118	120	129	105	143	177
Contraction, Per Cent	14	21	36	37	45	49
Obs. Oil, cc./m.³ (Tot. Gas at 32 Deg. F.)		4	41	61	63	66
Obs. H_2, cc./m.³ (Tot. Gas at 32 Deg. F.)	9	13	16	38	26	40
Primary Oil, cc./m.³			31	46	42	46
Per Cent CO converted					88	
Per Cent $CO \rightarrow CO_2$					29	
Feed Gas, Vol. Per Cent:						
CO_2		7.2			4.4	
H_2		59.7			57.1	
CO		31.3			37.1	
Residual		1.8			1.4	
H_2/CO		1.9:1.0			1.5:1.0	
Mol. Weight		14			14	
Product Gas, Vol. Per Cent:						
CO_2					27.6	
CO					8.6	
Unsaturates					2.7	
Oil Inspections:						
Mol. Weight					130	
Monoolefins, Mol. Per Cent					40	
Wax, Weight Per Cent					4.1	
Wax, M. P., °F.					149	
H_2O Inspections:						
H_2O, K. F. R., Weight Per Cent					79	
Acidity (Weight Per Cent CH_3COOH)					2.6	

Table X shows the wax and carbon formation on the cataylst after use for over 200 hours.

Table X

Catalyst No.	Oil+Wax, Weight Per Cent	Wax, M. P., °F.	Carbon, Weight Per Cent
395-1	5.1	241	5.8

Several catalysts were prepared in a similar manner to the catalyst of Example IV with the addition of a carbon inhibitor after calcining. Such carbon inhibitors incorporated into the catalyst before reduction but after calcination were $SnCl_4$, and $Pb(NO_3)_2$. The compositions of these catalysts and the results are shown in Table XI along with other catalysts prepared in a similar manner as the catalysts No. 395–1 of Example IV. Aside from the reported analysis of the catalysts, a small amount of titania, silica, and alumina, usually less than two or three per cent by weight total, is present in the ultimate catalyst as previously discussed. Unless otherwise specified aluminum was incorporated into the catalyst as $AlCl_3.6H_2O$ and reported as Al_2O_3 in all instances. Similarly, the potassium content of the catalyst was reported in all instances as K_2O.

Table XI

Cat. No.	Original Mixture, grams			Catalyst Composition, Parts by weight—Iron=100	
	Alan Wood Ore	K_2CO_3[1]	$AlCl_3.6H_2O$	K_2O	Al_2O_3
373.6	500	7.9	130.5 $[Al(COOH)_3]$	1.5	3.0
373.7	500	5.3	50.7	1.0	3.0
373.8	500	7.9	50.7	1.5	3.0
373.12	13,600	2.6	2,160 $[Al(NO_3)_3.9H_2O]$	1.5	3.0
374-1	500	7.3	110 $[Al(NO_3)_3 9H_2O]$	1.0	3.0
378-1	500	4.7	500	1.0	1.6
382-1	500	7.9	84.9	1.5	5.0
383-1	500	7.9	33.7	1.5	2.0
384-1	500	7.9	50.7 0.94 $SnCl_5H_2O$[1]	1.5	3.0 0.1 SnO
385-1	500	7.9	50.7 0.53 $Pb(NO_3)_2$[1]	1.5	3.0 1.1 PbO
390-1	500	7.9	16.5 $Ti(NO_3)_4$	1.5	3.0 TiO_2
391-1	500	7.9	30.5 $SiCl_4$	1.0	3.0 SiO_2
392-1	500	15.7	84.9	3.0	5.0
393-1	500		84.9 6.6 Rb_2CO_3[1]		5.0 1.5 Rb_2O
394-1	500		84.9 6.2 Cs_2CO_3[1]		5.0 1.5 Cs_2O
399-1	500	3.6	21.3 $Cu(NO_3)_2 3H_2O$	1.0	2.0 CuO
402-1	500	7.9	54 $Cu(NO_3)_2 3H_2O$	1.5	5.0 CuO
403-1	500	7.9	70.7 54 $Cu(NO_3)_2 3H_2O$	1.5	3.0 5.0 CuO
397-1	500		68.1 $Co(NO_3)_2$ 11.3 $Th(NO_3)_4$		3.0 CoO 1.5 ThO_2

[1] Added after calcination.

Cat. No.	Operating Conditions and Results, 250 p. s. i. pressure								Catalyst after about 250 hours	
	Calcination Temp., °F.	Reduction Temp., °F.	Gas Rate, V./Hr./V	Temp., °F.	Obs. Oil, cc./m.[3]	H_2O, cc./m.[3]	Per Cent $CO \rightarrow CO_2$	Per Cent Conv.	Wax, Weight Per Cent	Carbon, Weight Per Cent
373.6	1,400	1,475	228	580	123	95	31	98	7.9	2.3
373.7	1,410	1,475	193	580	107	83	28	95	9.7	3.2
373.8	1,420	1,475	186	580	113	90	23	96	8.7	2.6
373.12	1,450	1,480	215	580	94	95	26	97	8.4	4.3
374-1	1,410	1,475	203	560	90	83	24	97	6.1	3.2
378-1	1,420	1,500	196	540	99	62			11.3	4.1
382-1	1,420	1,500	175	560	102	61	33	96	8.5	6.0
383-1	1,400	1,500	178	580	100	102	24	95	6.1	3.3
384-1	1,420	1,485	180	600	104	93	27	96	5.7	2.8
385-1	1,400	1,485	190	600	108	91			7.4	6.9
390-1	1,400	1,485	210	600	93	89	26	95	2.3	2.8
391-1	1,400	1,475	238	600	80	80	31	93	8.1	2.7
392-1	1,400	1,485	210	540	85	63	30	98	8.5	4.0
393-1	1,400	1,485	205	540	78	66	27	98	2.7	3.6
394-1	1,400	1,485	204	540	73	71	33	98	4.0	6.0
399-1	1,400	1,485	158	580	90	79	34	95	9.1	4.2
402-1	1,400	1,425	213	600	79	77	12	97	8.6	4.1
403-1	1,400	1,425	214	600	71	82	20	96	8.7	3.5
397-1		1,485	153	540	16	45	36	86	1.0	3.9

EXAMPLE V

About 50.7 grams of $AlCl_3.6H_2O$ was dissolved in 50 cc's of distilled water and 7.9 grams of K_2CO_3 was dissolved in 25 cc. of distilled water. The carbonate solution was added to the chloride solution with stirring. The combined solutions were then admixed with about 500 grams of powdered Alan Wood ore to form a paste. The paste was mixed thoroughly and dried overnight at about 250° F. The dried catalyst was pulverized in a ball mill and calcined at a temperature of about 1400° F. for two hours. The calcined material was moistened with about 40 cc's of distilled water and then dried before attempting to pellet. One weight per cent graphite was added to the dried catalyst as a lubricant for pelleting and the material was then pelleted into $\frac{3}{16}$ inch diameter pellets. The pellets of calcined material were charged to a hydrogenation recirculating furnace and reduced at a maximum temperature of about 1505° F. The temperature was maintained at 1475° for 1.5 hours after the formation of water ceased. The catalyst prepared in this manner contains by weight about 3 parts Al_2O_3, about 1.5 parts K_2O, small proportions of silica and titania present in the original ore, and 100 parts metallic iron. The catalyst was designated No. 380–1.

The catalyst thus prepared was charged to a reaction chamber in the usual manner and the temperature of the reaction chamber and catalyst was brought to 500° F. while the catalyst was present in an inert atmosphere, such as carbon dioxide or nitrogen. This catalyst was used over a period of about 300 hours, during which time the temperature was increased from about 500° F. to about 615° F. The mol ratio of hydrogen to carbon monoxide passing through the reaction chamber during the test varied from about 1.9:1 to about 2.1:1 and contained an average of about 10.3 and about 9.8 volume per cent carbon dioxide and low molecular weight hydrocarbons (e. g. CH_4 and C_2H_6), respectively. Table XII below shows operating conditions and results obtained with catalyst No. 380–1. Table XIII shows the amount of formation of wax and carbon on the used catalyst after about 300 hours.

Table XII

Total Hours of Operation	40	64	136	184	232	256	304
Pressure, p. s. i.	250						
Catalyst Temp., °F.	500	520	560	580	600	615	
Gas Rate, V./Hr./V.	171	161	174	174	188	211	201
Contraction	47	-----	46	47	47	51	61
Obs. Oil, cc./m.³ (Tot. Gas at 32° F.)	45	72	82	72	69	68	56
Obs. H_2O, cc./m.³ (Tot. Gas at 32° F.)	47	71	83	81	94	96	94
Prim. Oil, cc./m.³	35	49	37	25	24	25	13
CO converted	-----	-----	97	-----	-----	-----	-----
CO → CO_2	-----	-----	23	-----	-----	-----	-----
Feed Gas, Vol. Per Cent:							
CO_2			9.9			10.6	
H_2			52.8			53.6	
CO			27.5			26.0	
Res.			9.8			9.8	
H_2/CO			1.9:1.0			2.1:1.0	
Mol. Weight			14			14	
Product Gas, Vol. Per Cent:							
CO_2	-----	-----	30.2	-----	-----	-----	-----
CO	-----	-----	1.6	-----	-----	-----	-----
Unsaturates	-----	-----	6.0	-----	-----	-----	-----
Mol. Weight	17	22	-----	-----	-----	-----	-----
Oil Inspections, Distillation:							
I. B. P., °F.	-----	-----	100				
5%	-----	-----	114				
10%	-----	-----	124				
50%	-----	-----	226				
90%	-----	-----	432				
E. P.	-----	-----	714				
Mol. Weight	-----	-----	118				
Monoolefins, Mol. Per Cent	-----	-----	65				
Wax, Weight Per Cent	-----	-----	2.8				
Wax, M. P., °F.	-----	-----	156				
H_2O Inspections:							
H_2O, K. F. R., Weight Per Cent	-----	-----	92				
Acid, Weight Per Cent (CH_3COOH)	-----	-----	0.8				

Table XIII

Catalyst No.	Oil and Wax, Weight Per Cent	Wax, M. P., °F.	Carbon Weight, Per Cent
380-1	4.2	217	3.4

EXAMPLE VI

About 50.7 grams of $AlCl_3.6H_2O$ were dissolved in 50 cc. of distilled water and this solution was mixed thoroughly with about 500 grams of powdered Alan Wood ore to form a paste. The paste was dried overnight at about 250° F. The dried material was crushed to a powder and was further impregnated with a solution of K_2CO_3 prepared by dissolving 7.9 grams of K_2CO_3 in 75 cc. of distilled water. When stirred thoroughly to form a paste, the paste was dried at 250° F. for several hours. One per cent graphite was added to the dried material and it was pelleted into $\frac{3}{16}$ inch diameter pellets. The pelleted material was reduced in a gas fired hydrogen recirculating furnace at a maximum temperature of about 1450° F. The temperature was maintained above 1425° F. for 1.5 hours after the formation of water ceased. The composition of the catalyst prepared in this manner was about 3 parts by weight Al_2O_3, about 1.5 parts by weight K_2O, a small proportion of titania and silica present in the original ore, and 100 parts by weight metallic iron. The catalyst was designated No. 381–1. The catalyst thus prepared was used to hydrogenate carbon monoxide according to the conditions shown in Table XIV. The synthesis gas used contained hydrogen and carbon monoxide in a mol ratio of about 1.5:1 to 1.7:1. The CO_2 in the synthesis gas averaged about 4.3 volume per cent and the total light hydrocarbons and nitrogen averaged about 3.3 volume per cent. Table XV below shows the formation of wax and carbon on the catalyst after about 200 hours of use.

Table XIV

Total Hours of Operation	41	114	138	162	186	210
Pressure, p. s. i.	250					
Catalyst Temp., °F.	500	540	560	580	600	620
Gas Rate, V./Hr./V.	131	129	126	125	166	211
Contraction, Per Cent	15	31	34	37	39	44
Obs. Oil, cc./m.³ (Tot. Gas at 32° F.)	27	35	58	54	40	38
Obs. H_2O, cc./m.³ (Tot. Gas at 32° F.)	45	49	51	52	64	84
Prim. Oil, cc./m.³	11	13	23	18	10	7
CO converted, Per Cent	-----	-----	-----	-----	-----	96
CO → CO_2 Per Cent	-----	-----	-----	-----	-----	31
Feed Gas, Vol. Per Cent:						
CO_2	5.2		3.3		4.3	
H_2	54.0		56.7		60.1	
CO	36.3		35.4		34.8	
Residual	4.5		4.6		0.8	
H_2/CO	1.5:1.0		1.6:1.0		1.7:10	
Mol. Weight	-----		15		14	
Product Gas, Vol. Per Cent:						
CO_2	-----	-----	-----	-----	-----	27.3
CO	-----	-----	-----	-----	-----	2.4
Unsaturates	-----	-----	-----	-----	-----	3.3
Mol. Weight	15	16	19	19	20	21
Oil Inspections:						
Mol. Weight			130			
Monoolefins, Mol. Per Cent			62.6			
Wax, Weight Per Cent			2.6			
Melting Point, °F.			144			
H_2O Inspections:						
H_2O, K. F. R., Weight Per Cent			92			
Acid, Weight Per Cent CH_3COOH			0.5			

Table XV

Catalyst No.	Oil and Wax, Weight Per Cent	Wax, M. P. °F.	Carbon, Weight Per Cent
381-1	1.0	220	4.9

EXAMPLE VII

About 510 grams of thorium nitrate

$Th(NO_3)_1.4H_2O$

was dissolved in 700 cc. of distilled water and the solution was thoroughly mixed with 6,800 grams of powdered Alan Wood ore in a mechanical mixer to form a thick paste. The resulting paste was dried overnight at 250° F. The dried material was then crushed to a powder and was calcined at a temperature of about 1000° F. for about three hours in a muffle furnace. After calcination 7,024 grams of the material was mixed with 198 grams of K_2CO_3 and ball milled to produce a powder smaller than about 30 mesh. The resulting mixture was then fused in a similar manner to that in Example I. The molten mass was cooled to form a solid mass. The solidified material was crushed and ball milled to produce a powder of the desired size, between about 8 and 12 mesh. The fused material was charged to a hydrogen recirculating furnace for reduction with hydrogen. The reduction was carried out over a period of five hours. The average reduction temperature was about 1445° F. and the maximum temperature observed was 1475° F. The formation of water terminated about one hour before the end of the reduction period. This catalyst was designated No. 423–1 and had a

composition by weight of 5 parts ThO_2, 1.5 parts K_2O, and about 100 parts iron. The catalyst was cooled in hydrogen and blanketed in carbon dioxide for transfer to the reaction chamber. The reaction chamber was brought to initial testing condition of 500° F. and 250 lbs. per square inch. The operation for the synthesis of organic compounds with hydrogen and carbon monoxide was carried out over a period of about 200 hours during which time the catalyst was tested at a temperature varying from 500° F. to 620° F. The composition of the synthesis feed gas used during operation was a mol ratio of about 1.4:1 of hydrogen to carbon monoxide. The carbon dioxide content of the feed gas varied from 1.6 to 2.9 volume per cent while the volume of low-boiling hydrocarbons and nitrogen varied from 4.5 to 5.0 volume per cent. Table XVI below shows operating conditions and the results obtained with this catalyst. Table XVII shows the formation of carbon and wax on the used catalyst after about 200 hours use.

Table XVI

Total Hours of Operation	42	54	90	114	138	16	186
Pressure, p. s. i.	250						
Catalyst Temp., °F	500	520	540	560	580	600	620
Gas rate, V./Hr./V	165	197	199	195	231	234	242
Contraction, Per Cent	48	47	46	56	58	60	60
Obs. Oil, cc./m.³ (Tot. Gas at 32° F.)	52	80	50	87	98	94	91
Obs. H_2O, cc./m.³ (Tot. Gas at 32° F.)	29	51	42	63	75	77	80
Prim. Oil, cc./m.³	44	61	35	71	77	77	70
Per Cent CO converted	----	----	----	----	97	----	----
Per Cent CO→CO_2	----	----	----	----	27	----	----
Feed Gas, Vol. Per Cent:							
CO_2	2.9					1.6	
H_2	53.2					53.9	
CO	39.5					39.5	
Residual	4.4					5.0	
H_2/CO	1.4:1.0					1.4:1.0	
Mol. Weight	14					14	
Product Gas, Vol. Per Cent:							
CO_2					32.5		
H_2					45.2		
CO					3.1		
CH_4					16.0		
C_2					3.2		
Mol. Weight					21		
Oil Inspections, Distillation:							
I. B. P., °F							
5%					172		
10%					206		
50%					385		
90%					676		
E.P.							
Mol. Weight					170		
Monoolefins, Mol. Per Cent					63		
Wax, Weight Per Cent					8		
Melting Point, °F					197		
H_2O Inspections:							
H_2O, K. F. R., Weight Per Cent					89		
Acid (Weight Per Cent CH_3COOH)					2.4		

Table XVII

Catalyst No.	Oil and Wax, Weight Per Cent	Wax, M. P., °F.	Carbon, Weight Per Cent
423-1	4.8	245	4.5

A catalyst prepared in a similar manner to the catalyst No. 423-1 but using manganese nitrate instead of thorium nitrate had a composition of about 5 parts by weight MnO, about 1.5 parts K_2O, and 100 parts metallic iron (small proportion of silica, alumina, and titania also present from original ore). This catalyst under similar operating conditions as the previous catalyst produced 119 cc./m.³ of oil and about 75 cc./m.³ of water.

EXAMPLE VIII

Several hundred grams of powdered Alan Wood ore were fused in the electric fusion apparatus of Example I to form a molten mass. The molten mass was cooled and solidified. The solidified mass was crushed in a jaw crusher and then ball milled to a size substantially less than 30 mesh. The pulverized fused Alan Wood ore was then pelleted to about ¼ inch diameter pellets in preparation for reduction. The pelleted Alan Wood ore was reduced with hydrogen at about 1100° F. for about 50 hours until the formation of water ceased. The reduced Alan Wood ore catalyst was charged to a reaction chamber in an atmosphere of carbon dioxide. The reaction chamber and catalyst were brought to a temperature of about 500° F. and then synthesis gas comprising hydrogen and carbon monoxide in a mol ratio of about 2:1 was introduced into the reaction chamber. A pressure of approximately 250 pounds per square inch was maintained during the run. Operating conditions and results obtained by the hydrogenation of carbon monoxide with this fused catalyst are shown in Table XVIII below. Table XIX shows the accumulation of wax and carbon from the catalyst after about 200 hours of use. This catalyst was designated No. 256.

Table XVIII

Total hours operation	121	145	168
Pressure, p. s. i.	250		
Catalyst Temp., °F	497	511	516
Gas Rate, V./Hr./V	105	93	94
Per Cent Concentration	26	29	30
Obs. Oil, cc./m.³ (Tot. gas at 32° F.)	42	47	42
H_2O cc./m.³ (Tot. gas at 32° F.)	62	59	51
Per Cent CO converted	45	60	65
Per Cent CO → CO_2	6	12	18
Feed Gas, Vol. Per Cent:			
CO_2	1.2		
H_2	65.4		
CO	30.4		
Residual	3.0		
H_2/CO	2.2:1.0		
Mol. Weight	12.1		
Product Gas, Vol. Per Cent:			
CO_2	3.9	6.7	9.6
Unsaturates	1.0	0.8	0.6
CO	23.3	18.2	15.9
Mol. Weight	13.5	14.1	14.7
Oil Inspections:			
Sp. Gr.	0.756		
Mol. Per Cent, Monoolefins	23		
H_2O Inspections:			
H_2O, K. F. R., Weight Per Cent	90.9		
Acid (Weight Per Cent CH_3COOH)	0.1		

Table XIX

Catalyst No.	Weight Per Cent Oil and Wax	Weight Per Cent Carbon
256	0.2	0.7

EXAMPLE IX

Four commercial ammonia synthesis catalysts obtained commercially from different sources were reduced at about 1500° F. until the formation of water ceased. The reduced commercial synthesis catalysts were then charged to a re-

action chamber and a gaseous mixture comprising hydrogen and carbon monoxide was passed therethrough. The original synthesis catalyst comprised substantially Fe_3O_4. The hydrogenation of carbon monoxide with these reduced ammonia synthesis catalysts was carried out at a pressure of about 250 pounds per square inch gage and under similar conditions described in the previous examples. Table XX below shows the operating conditions and results obtained with the reduced ammonia synthesis catalyst for the hydrogenation of carbon moxonide. It should be noted that the catalysts prepared according to this invention with Alan Wood ore compared favorably with the reduced ammonia systhesis catalysts in the production of organic compounds by the hydrogenation of carbon monoxide. With the catalysts of this invention, the selectivity and the yield of hydrocarbons having more than one carbon atom per molecule and oxygenated organic compounds are greatly superior in some instances to that of the reduced ammonia synthesis catalysts.

Table XX

NH_3 Synthesis Catalyst	Operating Conditions and Results							Catalyst Composition		
	Reduction Temp., °F.	Gas Rate, V./Hr./V.	Temp., °F.	Obs. Oil, cc./m.³	Water, cc./m.³	$CO \rightarrow CO_2$, Per Cent	Conv., Per Cent	Oil, Weight Per Cent	Carbon, Weight Per Cent	Hours
290-3	1,100	105	510	67	60	24	95	3.3	2.0	100
246-1	1,500	144	575	133	69	18	85	6.8	5.3	200
247-5	1,500	185	590	108	95	22	95	4.5	4.2	200
211-5	1,500	150	500	80	66	28	90	10.2	4.9	300

In all catalyst compositions reported herein, the iron after reduction was reported as Fe. The reduction process may not completely reduce the iron oxides to Fe and, consequently, small proportions of the iron may be present in other forms. The catalyst compositions also reported only the added ingredients in preparing the catalyst. Thus, such materials as silica, alumina, and titania will be present to some extent in the catalyst in all cases where Alan Wood ore was the source of the iron compound raw material whether or not actually reported.

Having described our invention, we claim:

1. A method for manufacturing a catalyst containing metallic iron as the major component for the hydrogenation of carbon monoxide to produce organic compounds which comprises admixing a naturally occurring magnetite with an aqueous solution of a material comprising a promoter to form a paste, drying the resulting paste at a temperature between about 200° F. and about 300° F. for at least two hours, calcining the resulting dried material at a temperature between about 1000° F. and about 1600° F. for at least two hours, cooling the calcined material, thereafter admixing the calcined material with an aqueous solution of a potassium compound containing oxygen to form a paste, drying the resulting paste at a temperature between about 200° F. and about 300° F. for at least two hours, pelleting the dried material, reducing the pelleted material with hydrogen at a temperature between about 1400° F. and about 1500° F. until the formation of water substantially ceases, and repulverizing the reduced pellets in an atmosphere of carbon dioxide.

2. A method for manufacturing a catalyst containing metallic iron as the major component for the hydrogenation of an oxide of carbon to produce organic compounds which comprises admixing a naturally occurring magnetite with a material comprising a promoter, calcining the resulting mixture at a temperature between about 1000° F. and about 1600° F. for at least two hours, pelleting the calcined material, reducing the pelleted material with hydrogen at a temperature between about 900° F. and about 1600° F. until the formation of water substantially ceases, and repulverizing the reduced pellets in a substantially inert atmosphere.

3. A method for manufacturing a hydrogenation catalyst containing metallic iron as the major component for the hydrogenation of an oxide of carbon to produce organic compounds which comprises admixing a naturally occurring magnetite with a minor amount of a material comprising at least one promoter, calcining the resulting mixture at a temperature above about 1000° F. for at least about two hours, cooling the calcined mixture, admixing the calcined mixture with a minor amount of a compound containing oxygen selected from the group consisting of an alkali metal and an alkaline earth, fusing the resulting mixture at a temperature of at least 2000° F. to form a molten mass, cooling the resulting molten mass sufficiently to solidify the same, grinding the molten mass to a size smaller than about 30 mesh, pelleting the resulting finely divided material to a size between about ⅛ inch and about ½ inch in diameter, reducing the pelleted mass with hydrogen at a temperature between about 900° F. and about 1600° F. until the formation of water substantially ceases, and repulverizing the reduced pellets in an atmosphere of carbon dioxide.

4. A method for manufacturing a catalyst containing metallic iron as the major component which comprises calcining a naturally occurring magnetite at a temperature between about 1000° F. and about 1600° F. for at least about two hours, pulverizing the calcined material to the desired size, and subsequently reducing the calcined material with hydrogen at an elevated temperature between about 900° F. and about 1600° F.

5. A method for manufacturing a catalyst containing metallic iron which comprises calcining a naturally occurring magnetite at a temperature between about 1000° F. and about 1600° F. for at least about two hours, pulverizing the calcined material to the desired size, and subsequently reducing the calcined material with hydrogen at an elevated temperature.

6. A method for manufacturing a catalyst containing metallic iron which comprises admixing magnetite with a promoter, calcining the resulting mixture at a temperature above about 1000° F. for at least about two hours, pulverizing the calcined material to the desired size, and subsequently reducing the calcined material with hydrogen at an elevated temperature.

7. In the method of claim 6 maintaining the

temperature of calcination between about 1400 and about 1600° F. and the time of calcination between about 2 and about 12 hours.

8. A method for manufacturing a hydrogenation catalyst containing metallic iron which comprises calcining a naturally occurring magnetite at a temperature above about 1000° F. for at least about 2 hours, fusing the calcined mixture at a temperature of at least 2000° F. to form molten mass, pulverizing the fused material and subsequently reducing the fused material with hydrogen at an elevated temperature.

9. A method for manufacturing a catalyst containing metallic iron which comprises calcining a mixture of magnetite and a promoter at a temperature above about 1000° F. for at least about 2 hours, and reducing the calcined material with hydrogen at an elevated temperature.

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Certificate of Correction

Patent No. 2,543,327 February 27, 1951

HENRY G. McGRATH ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 11, Table I, first column thereof, last line, for "CH_1COOH" read CH_3COOH; column 23, line 26, Table XVI, seventh column thereof, for "16" read *162*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of July, A. D. 1951.

[SEAL]

ERNEST F. KLINGE,
Assistant Commissioner of Patents.