PATENT SPECIFICATION

631,457

Application Date: Aug. 6, 1946. *No. 23324/46.*

Complete Specification Accepted: Nov. 3, 1949.

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Index at acceptance:—**Class 2(iii), B1g.**

COMPLETE SPECIFICATION

An Improved Process for the Catalytic Synthesis of Hydrocarbons

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation

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SPECIFICATION No. 631,457

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Standard Oil Development Company, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office in Linden, New Jersey, and 100, West 10th Street, Wilmington, Delaware, both in the United States of America.

THE PATENT OFFICE,
22nd April, 1950.

DS 32052/1(5)/3372 150 4/50 R

This invention relates to the catalytic conversion of carbon oxides with hydrogen to form valuable synthetic products. More specifically, the invention is concerned with improved catalysts and methods of operation for the catalytic synthesis of normally liquid hydrocarbons from CO and H_2.

The conventional hydrocarbon synthesis processes may be divided into two broad classes, depending on the type of catalyst used and the character of reaction products obtained. One class comprises reactions carried out at relatively low temperatures of about 350°—450° F. and relatively low pressures of about 1—10 atm. abs. in the presence of catalysts of which cobalt is a typical representative to form predominantly saturated paraffinic liquid and solid hydrocarbons from which highly valuable diesel fuels and lubricating oils but only low octane number motor fuels may be obtained. The other class of processes employs iron type catalysts at higher temperatures of about 450°—800° F. and higher pressures of about 3—25 atm. abs. to obtain a predominantly unsaturated product from which highly valuable motor fuels having satisfactory octane ratings may be recovered.

In contrast to the above hydrocarbon synthesis processes, with which the

[*Price 2/-*]

or oxides thereof which are reduced to the metal under the conditions of working; or yet again a reduced and sintered mixture of a precipitated iron compound to which has been added a precipitated compound of another metal, for example beryllium, manganese, or zinc, which on heating yields an oxide not reducible by hydrogen to metal below 900° C.

More conventional iron catalysts are those prepared by the reduction of various iron ores or precipitated iron oxides as well as by the decomposition of iron carbonyls. The catalytic activity of the iron may be enhanced by the addition of such promoters as various compounds of alkali metals or the oxides of chromium, zinc, aluminium, magnesium, manganese, the rare earth metals, and others, in small amounts of about 1—10%. It has also been suggested to deposit these iron catalysts on inert or active carriers such as siliceous materials, particularly kieselguhr, pumice, synthetic silicon gel, or hydrated alumina.

The last-mentioned catalysts, that is those supported on carriers, have been found to be of particular interest in connection with synthesis reactions employing the so-called fluid catalyst technique wherein the synthesis gas is contacted with a dense turbulent bed of finely-divided catalyst fluidized by the gaseous

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LONDON

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An Improved Process for the Catalytic Synthesis of Hydrocarbons

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America.)

I, JOHN CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the catalytic conversion of carbon oxides with hydrogen to form valuable synthetic products. More specifically, the invention is concerned with improved catalysts and methods of operation for the catalytic synthesis of normally liquid hydrocarbons from CO and H_2.

The conventional hydrocarbon synthesis processes may be divided into two broad classes, depending on the type of catalyst used and the character of reaction products obtained. One class comprises reactions carried out at relatively low temperatures of about 350°—450° F. and relatively low pressures of about 1—10 atm. abs. in the presence of catalysts of which cobalt is a typical representative to form predominantly saturated paraffinic liquid and solid hydrocarbons from which highly valuable diesel fuels and lubricating oils but only low octane number motor fuels may be obtained. The other class of processes employs iron type catalysts at higher temperatures of about 450°—800° F. and higher pressures of about 3—25 atm. abs. to obtain a predominantly unsaturated product from which highly valuable motor fuels having satisfactory octane ratings may be recovered.

In contrast to the above hydrocarbon synthesis processes, with which the present invention is concerned, a synthesis process of a different type comprises the production of oxygenated hydrocarbons, especially methanol, by the use of extremely high pressures, for example 200 atmospheres and higher and temperatures in the range of 300°—400° C. and a suitable catalyst such as an iron spinel catalyst with or without the addition of alkali or alkali metal compounds.

In the hydrocarbon synthesis process catalysts comprising iron in admixture with another metal have been proposed. For instance iron or a compound thereof together with copper, silver, gold or zinc or oxides thereof which are reduced to the metal under the conditions of working; or yet again a reduced and sintered mixture of a precipitated iron compound to which has been added a precipitated compound of another metal, for example beryllium, manganese, or zinc, which on heating yields an oxide not reducible by hydrogen to metal below 900° C.

More conventional iron catalysts are those prepared by the reduction of various iron ores or precipitated iron oxides as well as by the decomposition of iron carbonyls. The catalytic activity of the iron may be enhanced by the addition of such promoters as various compounds of alkali metals or the oxides of chromium, zinc, aluminium, magnesium, manganese, the rare earth metals, and others, in small amounts of about 1—10%. It has also been suggested to deposit these iron catalysts on inert or active carriers such as siliceous materials, particularly kieselguhr, pumice, synthetic silicon gel, or hydrated alumina.

The last-mentioned catalysts, that is those supported on carriers, have been found to be of particular interest in connection with synthesis reactions employing the so-called fluid-catalyst technique wherein the synthesis gas is contacted with a dense turbulent bed of finely-divided catalyst fluidized by the gaseous

[*Price* 2/-]

reactants and products and which permits continuous catalyst replacement and affords a greatly improved temperature control of the highly exothermic and temperature-sensitive synthesis reaction. The adaptation of the hydrocarbon synthesis to the fluid catalyst technique has introduced a new factor in the rating of synthesis catalysts. While total liquid yield as determined by activity (per cent. conversion) and selectivity (ratio C_4+ higher hydrocarbons: C_1+higher hydrocarbons), olefin formation, and catalyst stability are the essential characteristics determining the utility of fixed bed synthesis catalysts, the fluid technique requires, in addition, ease of fluidization. None of the prior art catalysts complies satisfactorily with these requirements. Unsupported iron catalysts, while exhibiting high activity and selectivity, have poor fluidization characteristics mainly due to their high bulk density. The known carrier catalysts have superior fluidization characteristics but fall short with respect to activity and selectivity. This situation has stimulated extensive research to develop a new type of synthesis catalyst of equal utility for fixed bed and fluid catalyst technique. The present invention includes such new development.

It is, therefore, a principal object of the present invention to provide a process for synthesizing hydrocarbons from hydrogen and oxides of carbon in the presence of an improved synthesis catalyst.

It is a more specific object of the invention to provide an improved hydrocarbon synthesis process carried out in the presence of a carrier catalyst having utility for both fixed bed and fluid operation.

A further object of the present invention is to provide a synthesis process of the type specified which is carried out in the presence of an improved iron type catalyst supported on a carrier material.

Another object of the invention is to provide means for improving the operation and efficiency of the catalytic synthesis of high-octane motor fuels from CO and H_2, employing the fluid catalyst technique.

A still further object of the invention is to provide improved catalysts for the hydrocarbon synthesis, having utility for both fixed bed and fluid operation.

Other and further objects and advantages will appear hereinafter.

It has been found that these objects may be accomplished quite generally by carrying out the synthesis reaction in the presence of a catalyst which comprises the oxide of trivalent iron, that is Fe_2O_3, in combination with an equimolecular proportion of one or more oxides of one or more bivalent metals other than iron. Reduction products of these oxide composites may likewise be used. Investigations indicate that the superior qualities of these catalysts are due to the formation of particularly active spinel-type compounds having the general formula $Me^{++}Fe_2^{+++}O_4$, wherein Me^{++} is a bivalent metal other than iron and Fe^{+++} is trivalent iron. The bivalent metal component is therefore selected from those metals and metal compounds which on the basis of their chemical and physical characteristics are capable of forming spinel-type compounds with the oxide of trivalent iron. Examples for such bivalent metals are Mg, Zn, Mn, Cd, the alkaline earth metals, Be and Cu. In accordance with the present invention the bivalent metal component is used in proportions at least sufficient to convert the total amount of trivalent iron present into a spinel-type compound (i.e. at least equimolecular proportions with respect to the Fe_2O_3). Larger amounts of bivalent metal component acts as diluent or carrier without adversely affecting the activity of the spinel-type combination proper. Therefore by using an excess of a bivalent component giving a relatively low bulk density such as MgO, catalysts of excellent utility for fluid solids operation may be prepared.

The bivalent metals other than iron mentioned above give with trivalent iron oxide when used in spinel-forming proportions, composites having a high synthesizing activity at least approximating and mostly surpassing that of pure iron catalysts including magnetite which is a naturally occurring iron spinel having the formula $Fe^{++}Fe_2^{++}{}^{+}O_4=F_3O_4$. However, particularly good results are obtained when using Mg and/or Zn as the bivalent metal component. Materials comprising oxide composites of trivalent iron with at least spinel-forming proportions of Mg and/or Zn, or reduction products of these oxide composites are, therefore, the preferred synthesis catalysts. As indicated above the bivalent component of the catalyst may comprise oxides of one or more of the bivalent metals described.

The addition of a promoter and a stabilizer greatly enhances the activity of the catalysts. Preferred promoters are those obtained by the addition, to the original catalyst composite, of compounds of potassium, such as KOH, K_2CO_3, KNO_3, KCl and K_2O. Similar compounds of other alkalies such as Na, and Li, or of Ba and Ca, as well as oxides of such elements as Al, Si, Cu, Mn or Cr may be added as promoters. Useful stabilizers may be derived from the oxides of metals of the right hand side (transition series) of Groups I, II and III of the Periodic System. CuO has been found to be particularly suitable for this purpose. The principal function of the promoter is to increase catalytic activity while the stabilizer is added to prevent deactivation of the catalyst.

The catalysts may be prepared by methods of coprecipitation, impregnation or wet mixing, in any conventional manner, followed by drying, pilling and roasting at temperatures of about 800°—1600° F. to obtain the catalyst in the oxide form which, if desired, may be reduced with a reducing gas, preferably hydrogen, at temperatures of about 600°—1800° F. Satisfactory results are obtained with catalysts containing, prior to reduction, from about 10 or 20%, to 80%, preferably about 30—80%, by weight of Fe_2O_3 when magnesium oxide is the bivalent component, and from about 5—65%, preferably 25—50% by weight of Fe_2O_3 when zinc oxide is the bivalent component. The proportions of Fe_2O_3 in combination with other bivalent components vary depending on the molecular weights involved. Promoter and stabilizer may be added in proportions varying from 0.1—10% and 1—20%, respectively based on the composite catalyst. Excellent yields of valuable liquid hydrocarbons have been obtained for example with a catalyst composed as follows:—

MgO	-	-	54%
Fe_2O_3	-	-	40%
CuO	-	-	5%
K_2O	-	-	1%

A typical method suitable for preparing catalysts is as follows:—

Magnesia is mixed with a solution of ferric nitrate. Ammonium hydroxide may be added to ensure complete precipitation. The magnesia with ferric hydroxide precipitate is washed and then mixed with solutions of copper nitrate and potassium nitrate. The resulting mixture is dried, molded into pills or lumps of any suitable size and shape, roasted at about 1000° F., reduced for about four hours at about 900° F. with about 1000 V/V/hr. of excess hydrogen and sintered for about four hours at about 1200° F. in a non-oxidizing atmosphere, of for example hydrogen.

In carrying out the hydrocarbon synthesis in the presence of catalysts of the type above described, conventional synthesis conditions for iron catalysts may be employed, for example temperatures of about 450°—800° F., preferably 500°—700° F., pressures of about 3—25 atm., H_2:CO ratios of about 0.6:1—3:1, and space velocities of about 100—2500 V/V/hr. in either fixed bed or fluid bed operation. In the latter case the catalysts may have a particle size falling within the wide range of 5—500μ diameter while spheres of 5—200μ diameter are preferably used at superficial gas velocities of 0.3—5 ft. per second.

The superiority of the new type iron spinel catalysts over a pure iron catalyst such as the $Fe^{++}Fe^{+++}$ spinel magnetite in the absence of carriers and promoters is illustrated by the typical experimental data listed in Table I below, which were obtained at optimum reaction temperature for the individual catalysts.

TABLE I.

	1 Mol. Fe_2O_3 +			
	1 mol. MgO ($MgFe_2O_4$)	1 mol. ZnO ($ZnFe_2O_4$)	1 mol. CaO ($CaFe_2O_4$	1 mol. FeO (Magnetite)
Catalyst Reduction	4 hours with 1000 V/V/hr. Excess H_2			
Catalyst reduction tem. °F. -	900°	900°	900°	900°—1200°
Synthesis gas feed rate, V/V/hr.	200			
Synthesis press., psig.	250			
Synthesis temp. °F. - - -	530°	535°	567°	574°
H_2:CO volume ratio in synthesis feed gas - - - -	1:1	1:1	1:1	1:1
Vol. % CO_2 in exit gas - -	48	49	46	29
% CO conversion - - -	96	96	94	78
Measured yield (c.c./cu.m.feed)	144	102	80	77
Yield of C_4 and higher hydrocarbons (c.c./cu.m. H_2+CO consumed) - - -	203	170	145	142

The above data show that the spinel-type catalysts of the present invention give a CO conversion which is by more than 20% higher than that obtainable when using pure iron spinel. Of particular importance are the high yields of liquid products produced by the zinc and magnesium spinels which surpass those of magnetite by more than 20% and 40%, respectively.

As indicated above a further advantage of the catalysts of the present invention resides in the fact that they may be supported on an excess of bivalent component to obtain supported catalysts of highest activity suitable for the hydrocarbon synthesis employing the fluid solids technique.

The data of Table II below illustrate the advantages of the use of the new catalysts over procedures using iron catalysts supported on different carriers such as alumina, silica microspheres, and silica-alumina microspheres, and iron catalysts free of carrier material. A series of tests carried out on such miscellaneous catalysts at 250 lbs./sq. in. pressure, 200 V/V/hr. space velocity, an 0.8—1.1 $H_2:CO$ feed ratio and optimum reaction temperatures for the individual catalysts yielded the following results for fixed bed operation.

TABLE II.

Catalyst Composition Prior to Reduction at 900° F. and Sintering at 1200° F.	Max. Measured Liquid Yield, cc./cu.m. Synthesis Gas (Input Basis)	Temp. °F.	Conv. % *
54% MgO, 40% Fe_2O_3, 5% CuO, 1% K_2O	126	517	90
90% Fe_2O_3, 10% Al_2O_3 (mixed ppt.)	72	547	90
69% Al_2O_3, 30% Fe_2O_3, 1% KCl	44	592	75
68% Fe_2O_3 on 32% alumina-silica microspheres	39	552	70
45% Fe_2O_3 on 55% silica microspheres	21	628	72
Red Fe_2O_3 + 1% KCl	139	517	96

* Estimated

From the above data it will be seen that the process carried out in the presence of magnesia-supported iron-magnesia spinel catalyst promoted with potassium and copper yields about 75% more liquid hydrocarbons than the process using the most active of the other carrier catalysts tested and closely approaches the yields obtainable with pure iron oxide promoted with KCl.

Fluidity tests carried out in a 1—⅛" fused silica tube using H_2 or N_2 as the fluidizing gas at superficial velocities of 0.3—0.5 ft. per second gave the following results:—

TABLE III.

Catalyst	Size Microns	Bulk Density	Fluidity at 600° F.
54% MgO, 40% Fe_2O_3, 5% CuO, 1% K_2O	5—125	0.90	Good
32% alumina-silica hydrogel, 68% Fe_2O_3	50—60	0.79	Good
55% silica gel, 45% Fe_2O_3	5—125	0.62	Good
Hematite	5—75	2.4	Poor
Iron powder	5—75	2.4	Poor
Magnetite	5—75	2.4	Poor

The above table shows that the magnesia supported spinel catalyst of the present invention has the same good characteristics for use in fluid catalyst systems as other carrier catalysts and is in this respect greatly superior to pure iron catalysts. Other of the spinel-type catalysts supported in bivalent components of low bulk density have similar good fluidity characteristics.

From the foregoing, it will be readily appreciated that the improved synthesis catalysts combine highest activity and selectivity with satisfactory ease of fluidization. An additional advantage of the present invention resides in the fact that the yields of olefins are appreciably higher than those obtainable with other carrier catalysts at similar reaction conditions. This combination of characteristics distinguishes the catalysts of the present invention over any known prior art synthesis catalyst.

The present invention is not to be limited to any theory of the mechanism of the process or catalysts nor to any examples given merely for illustrative purposes.

Having now particuarly described and ascertained the nature of the said invention, and in what manner the same is to be performed, as commuicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen which comprises contacting a gas mixture containing carbon monoxide and hydrogen in synthesis proportions, under hydrocarbon synthesis conditions of temperature and pressure with a catalyst comprising a tri-valent iron oxide and at least an equimolecular proportion of one or more oxides of one or more bi-valent metals other than iron which will form a spinel type compound with the said iron oxide or products obtained by reducing such mixtures.

2. A process as claimed in Claim 1 wherein the bi-valent metal oxide is an oxide of manganese, magnesium, cadmium, zinc, alkaline earth metals, beryllium, copper, and the like, and preferably magnesium or zinc oxides.

3. A process as claimed in Claim 1 or 2 wherein the catalyst contains more than 1 molar proportion of the bi-valent oxide and the excess of such oxide is employed as a support or carrier for the catlyst composition.

4. A process as claimed in Claims 1—3 wherein the catalyst is a spinel type compound prepared from the oxides.

5 A process as claimed in any of the preceding claims wherein the catalyst comprises a mixture of from 80—20% of magnesium oxide and from 20—80%, and preferably from 30—80% of tri-valent iron oxide.

6. A process as claimed in any of the preceding claims 1—4 wherein the catalyst comprises a mixture of from 5—65%, and preferably from 25—50%, by weight of tri-valent iron oxide and from 95—35%, and preferably from 50—75%, of zinc oxide.

7. A process as claimed in any of claims 1—6 wherein the catalyst also contains from 0.1—10% of a catalyst promoter, for example, oxides, hydroxides, carbonates, nitrates, or chlorides of alkali metals, or oxides of aluminium, silicon manganese, copper and chromium, potassium oxide being the preferred promoter.

8. A process as claimed in Claim 7 wherein the catalyst also comprises from 1—20% of a catalyst stabilizer compound, for example, an oxide of a metal of the first, second, or third groups (right hand side) of the periodic system, and preferably copper oxide.

9. A process as claimed in any of the preceding claims wherein the catalyst is prepared by co-precipitating a mixture of solutions of salts of the metals and converting the precipitate obtained to the oxides.

10. A process as claimed in any of the preceding claims 1—8 wherein the catalyst is obtained by impregnating the oxide of one of the metals with a solution of a soluble salt of the other metal easily convertible into the oxide, and converting the same to the oxide.

11. A process as claimed in Claims 9 and 10 wherein the mixture of oxides obtained is subjected to roasting at an elevated temperature.

12. A process as claimed in any of claims 9—11 wherein the catalyst mixture is reduced at an elevated temperature of 600—1800° F. in the presence of hydrogen.

13. A process as claimed in any of Claims 9—12 wherein the catalyst is sintered before use.

Dated this 6th day of August, 1946.
D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicant.

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