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PATENT SPECIFICATION

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623,815

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3466

Index at acceptance:—**Class 1(i), F3b1.**

COMPLETE SPECIFICATION

Improvements in or relating to Catalysts for use in the Synthesis of Hydrocarbons

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 (a communication from 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 at Linden, New Jersey, United States of America), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to improved catalysts for the synthesis of hydrocarbons and oxygen-containing derivatives by reduction of carbon oxides with hydrogen and more specifically to an iron catalyst which is particularly efficient, cheap and readily available. The nature of this catalyst, method of manufacture and use will be fully understood from the following description.

In the accompanying drawing there is shown an apparatus for conducting the synthetic production of hydrocarbons and oxygenated derivatives by reduction of carbon oxides with hydrogen and the drawing indicates the flow of the materials through the process.

Heretofore iron bearing catalysts, particularly iron oxide catalysts, have been used for bringing about the reaction between carbon oxides, particularly carbon monoxide, and hydrogen to form liquid hydrocarbons with or without the production of oxygen-containing derivatives such as alcohols, acids and the like. It has been generally the practice to produce these catalysts from purified iron salts but these catalysts require a long period of activation before they are of real use and they are also relatively expensive.

It has now been found that excellent iron bearing catalysts can be produced from certain pyritic ores, for example, pyrite, marcasite and pyrrhotite. Fortunately these ores are of low grade and are not in great demand. They are usually roasted in presence of air to produce sulfur dioxide for the manufacture of sulfuric acid, and are quite cheap. The roasting treatment which is accomplished at the temperatures of 1800-2200° F. converts the iron sulfides into Fe_2O_3 which is then gently sintered. A typical analysis of such a roasted material is as follows:

Fe_2O_3	96.2%
Available oxygen	27.0%
Silica	1.5%
Sulfur	Less than .05%

This material after roasting is extremely hard but it can be ground to any desired size. If the finished catalyst is to be used in fixed bed reactors, it is preferred to reduce the roasted material to granular form by crushing or grinding. Granules of the size of 4-8 mesh are suitable for use in most fixed bed reactors. If the finished catalyst is to be used in a fluid reactor, the roasted material is ground to a powder of suitable particle size for fluidizing under synthesis conditions. The following particle size distribution has been found to be suitable for use in fluid type reactors:

Diameter	*Per cent.*
0 to 20 microns	5 to 25
20 ,, 80 ,,	30 ,, 85
Above 80 microns but still characterized as finely divided	5 ,, 45

After the roasted material has been obtained in the desired particle size for fixed bed or for fluid operation, as the case may be, it is impregnated with from 0.5 to 10% of a suitable promoter such as sodium carbonate, potassium carbonate, potassium chloride, potassium phosphate or alkali metal aluminates. In addition to the compounds of alkali metals listed above, other promoters such as copper, silver, nickel and thorium oxide may be used if desired. Instead of adding the promoters by impregnation, they may be mixed with the roasted ore and fused. The fused mass must then be broken down to the desired particle size. A-B.

In carrying out the process using the fluidized type of solid, the following des-

[*Price* 2/-]

cription of a suitable apparatus, diagrammatically illustrated by the accompanying drawing, may be of assistance:

Referring to the drawing, numeral 1 denotes a reaction vessel which is generally in the form of an upright cylinder with a conical base 2. A grid or screen 3 is located in the lower part of the cylinder so as to effect good gas distribution and in the upper portion of the cylinder a dust separator 4 is generally indicated. The separator is preferably of the type operating on centrifugal principles and the dust so separated is returned to the fluidized mass by the pipe 5 while the gas and vapor mixture is taken out by the pipe 6 to a scrubber condenser 7, fed with water by a pipe 8. The gas from which liquid products and final traces of catalyst have been removed is withdrawn by a pipe 9 and the liquid is separated in the vessel 10, water being withdrawn at the bottom by 11 and the hydro-carbon product by the pipe 12.

Within the reactor 1 it will be understood that the catalyst particles are distributed throughout the reacting gases in the form of a dense suspension, which comprises a denser phase below and a lighter phase above which are separated by a so-called interface or level which is indicated generally at 13. Within the denser phase cooling pipes 14 are located but it will be understood that they may be arranged in any preferred manner, not necessarily as shown.

Within this reactor the suspension is in vigorous motion which insures efficient utilization of the catalyst and accurate temperature control from top to bottom.

The gaseous feed consisting, for example, of a mixture of two parts of hydrogen to one part of CO is supplied by the pipe 15 through a heater 16 which is employed until the apparatus has been raised to reaction temperature. Thereafter the gas is preferably directed, or at least a part of it is directed around the heater by means of a pipe 16a and fed into the reactor below the grid 3. It will be understood that the reaction itself normally produces sufficient heat to maintain itself and, in fact, cooling by the pipes 14 will be required.

At intervals a portion of the catalyst may be withdrawn by a pipe 17 as indicated and the catalyst may be separated from the carrying gas and regenerated or reworked as desired. Fresh catalyst may be supplied by the pipe 18, preferably in a carrier gas which may be a portion of the feed gas.

Considerable variation may be made in the apparatus for carrying out the reaction in fluidized form but, in general, that shown in the drawing is suitable. In any case, it should consist of an enlarged vertical reaction vessel provided with cooling means. It should be fed at the bottom and the catalyst is preferably separated from the gas within the reaction shell so as to maintain the bulk of the catalyst always within the reactor and to withdraw a product gas. After the separation of the liquid product from the gas, the latter may be recirculated to the reaction chamber usually after a suitable adjustment of its composition.

In order to understand more fully the conditions of operation of the present process, it should be noted that in the fluidized type of reactor the gas velocity upward is adjusted so as to maintain the distribution of the catalyst particles throughout the gas in dense suspension. The velocity is preferably in the range from about .2 to 1.5 ft. per second, measured on the overall cross section of the reactor, and the upward velocity is sufficient to maintain the catalyst in suspension. The temperature and pressure conditions of the reactor depend to some extent on whether hydrocarbons alone are to be produced or if it is desired to produce oxygen containing materials as well. In general the temperature is from about 350° to 675° F. and it is preferred to use a pressure of 10 to 30 atmospheres, particularly for hydrocarbon production and even higher for the production of oxygenated materials.

In fixed bed operation the catalyst is used as mentioned above in granular form; the temperature and pressure conditions are substantially the same as given above.

The present catalyst is charged to the reactor whether of the type for fixed bed or fluidized operation and then should be reduced therein with hydrogen, preferably at a temperature from 550° to 1100° F. This is accomplished in a relatively short time and, as mentioned above, the catalyst does not have the long period of induction which is usually required with iron bearing catalysts. If the catalyst is intended for a fixed bed type reactor, the catalyst may be fitted in any known manner subsequent to the reducing treatment. To more clearly illustrate the nature of the present catalyst and its use, the following examples may be considered:

EXAMPLE 1

A catalyst was prepared from a sintered pyrite ash which contained 67.3% Fe and 27.0% available O_2 and less than 0.02% S by grinding to a powder and impregnating the powder with sodium carbonate solution so as to contain about .5% of the salt on drying. The product was dried at 240° F. and was then charged to a fluid-solid type reactor such as illustrated above.

The catalyst was reduced with hydrogen

at 700° F. for a period of about six hours and then fed directly with synthesis gas. The data given below include not only the data with this improved catalyst but also data typical of the iron bearing catalysts and obtained from published literature.

	Literature	*Present Catalyst*
H_2/CO in Fresh Feed	1.27/1	1.50/1
H_2/CO Consumed	1.26/1	1.40/1
Temperature °F.	608-626	600
Pressure Lbs./Sq. In.	300	275
Fresh Food Vols./Vol. of catalyst/Hr.*	270	996
CO Conversion	75	98
Carbon Balance	100	91
% CO to C_4+	41	47.4
Ratio C_4+/C_1+**	.62	.61
cc C_4+/cubic metres ($CO+H_2$) Consumed	163	182
Gallons C_4+/day/lb. of Catalyst	0.04	0.18

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*Measured at 32° F., 760 mm.

**Ratio of carbon in hydrocarbons in C_4 or higher fraction to carbon in total hydrocarbon product.

It should be noted that the pyrite ash catalyst required only a short reduction period and there was no induction period. The catalysts known in literature of this type usually required a long period of activation and are distinguished by an induction period of 2 to 5 days. It should also be noted that the CO conversion is considerably higher and the production of liquid hydrocarbons is better.

EXAMPLE 2

Fixed bed units for testing the activity of synthesis catalysts were employed to test the quality of a granular pyrite ash catalyst made as above and impregnated with 1/2% of sodium carbonate. The data on four runs of this material are given below:

Catalyst Form	⅛" Pills	6-8 Mesh	6-8 Mesh	6-8 Mesh
Reduction Temperature	700°F.	700°F.	900°F.	900°F.
Temperature of Run	575°F.	576°F.	586°F.	581°F.
Pressure Lbs./Sq. In.	250	240	249	250
Space Velocity in Vols./Vol. of Catalyst/Hr.*	212	198	195	206
Yields				
cc/meter³ ($CO+H_2$) Fed* Output	137	129	154	152
% CO Conversion	87	74	95	94
C_4+C_1**	.63	.66	.60	.63
Material Balance %(Yield as percentage by wt. of feed)	97	93	76	99

From the above table the high activity of this catalyst can be readily observed.

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*Measured at 32°F., 760 mm.

**Ratio of carbon in hydrocarbons in C_4 or higher fraction to carbon in total hydrocarbon product.

EXAMPLE 3.

The following data were obtained in a small fluid unit using roasted pyrite ore which had been impregnated with 1% potassium chloride.

The catalyst was ground to the size distribution specified in the specification above and it was charged into the unit, reduced therein with hydrogen and two runs of about 24 hours each were made, carefully observed and all the data collected as follows:

	A	*B*
Catalyst Reduction Temperature	671°F.	
Catalyst Temperature during Run, °F.	550	600
Reactor Pressure, Lbs./Sq. In.	277	275
H_2/CO in Fresh Feed by Volume	1.02	1.00
H_2/CO Consumed, Output	1.02	.97
Fresh Feed Rate, Vols./Vol. of Catalyst/H_1*	450	1040

% CO Conversion, Output	91	98
% Carbon Balance	88	96
% Converted CO to C_4+	43.6	40.8
Ratio C_4+/C_1+**	.70	.62
Output C_4+, cc/cubic metres H_2+CO Consumed	196	183
Gallons C_4+/day/lb. Catalyst	.08	.20

*Measured at 32°F., 760 mm.

**Ratio of carbon in hydrocarbons in C_4 or higher fraction to carbon in total hydrocarbon product.

The operation was smooth throughout, the yield excellent as seen from the above data.

The present catalyst is superior to other iron bearing catalysts, first, in respect to activity and selectivity in the direction of producing liquid hydrocarbons, and also in ability to produce only small proportions of methane and ethane, in superiority of the quality of the motor fuel produced and in respect to catalyst life. It is notable that this catalyst is superior in most respects to the purer iron bearing catalysts which are made directly from pure iron or from purified iron salts and from the oxide and carbonate ores. It is also superior to the less pure iron ore catalysts which have been employed.

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

1. An improved process for the catalytic synthesis of liquid organic compounds by reaction of carbon monoxide and hydrogen wherein the catalyst comprises a hydrogen reduced iron pyrite ash.

2. An improved process for the catalytic synthesis of liquid hydrocarbons and oxygen containing compounds by reaction of CO and hydrogen wherein the catalyst comprises a reduced iron pyrite ash impregnated with a promoting substance.

3. A process according to claim 2 in which the promoter is an alkaline substance.

4. A process according to claim 2 in which the promoter is an alkali halide.

5. A process according to claim 2 in which the promoter is potassium chloride.

6. An improved process for producing a catalyst for reaction of carbon monoxide and hydrogen which comprises roasting a pyrite ash, withdrawing sulfur dioxide, grinding the sintered ash so obtained to powder and reducing the same with hydrogen at an elevated temperature.

7. Process according to claim 6 in which the reduced ash is subsequently pilled.

8. An improved process for converting carbon monoxide and hydrogen to liquid hydrocarbons and oxygenated derivatives which comprises subjecting the gas mixture to contact with a reduced iron pyrite ash at a temperature of the range of 350 to 650° F. under superatmospheric pressure.

9. An improved process for preparing a catalyst for synthesis of hydrocarbons from carbon monoxide and hydrogen, which comprises roasting an iron sulphide ore in air under conditions of time and temperature to produce an ash containing less than 0.05% sulphur, reducing particle size to a desired range, adding a suitable promoter, and reducing with a gas rich in free hydrogen at an elevated temperature.

Dated this 23rd day of August, 1946.

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Agents for the Applicant.

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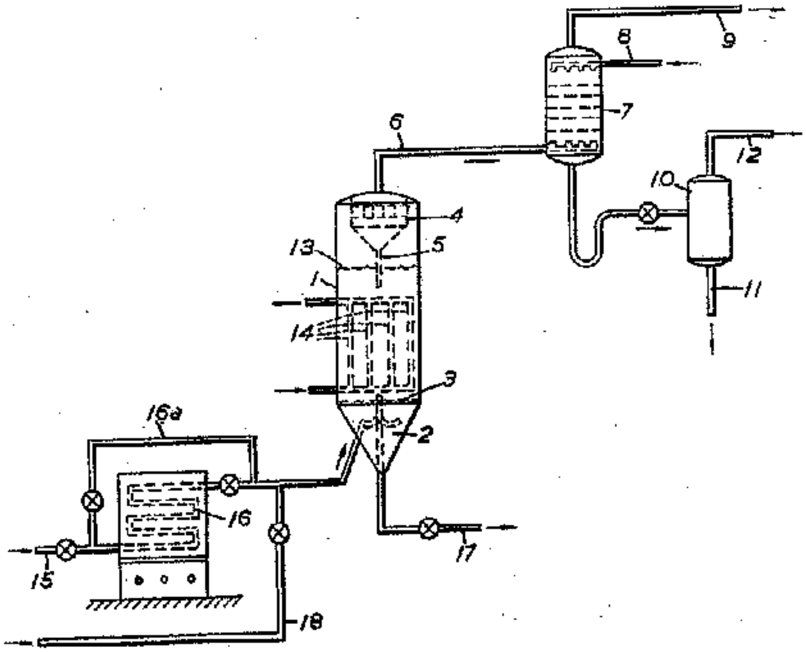
1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale.]



H.M.S.O.(Ty.P.)