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PATENT SPECIFICATION

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3555

COMPLETE SPECIFICATION.

Improvements in or relating to a Hydrocarbon Synthesis Process.

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, Elizabeth, New Jersey, United States of America, 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 :—

The present invention is concerned with a hydrocarbon synthesis process employing improved catalysts.

It is well known in the art to conduct hydrocarbon synthesis reactions by contacting hydrogen and oxides of carbon with catalysts under various temperature and pressure conditions. The catalyst employed is usually selected from the iron group metals, as for example, iron, cobalt and nickel. The catalyst are utilized either alone or are employed in conjunction with carriers, such as kieselguhr, diatomaceous earth, synthetic gels, silica, and alumina. Promoters, such as oxides of sodium, potassium, chromium, zinc, aluminium, magnesium and the rare earth metals are used with the iron group metals. These catalysts are employed in either fixed bed or fluid catalyst operations.

The temperatures employed in the synthesis reaction vary widely, as for example, in the range from about 300° F. to about 800° F. and are generally in the range from about 350° F. to about 750° F. The pressures, likewise, vary considerably and are a function of other operating conditions, such as catalyst employed, activity of the catalyst, character of the feed gases and the temperature utilized. Pressures in the range from about 1 to 100, and higher, atmospheres have been suggested. The character of the feed gases introduced into the synthesis reaction zone depends somewhat on the particular temperatures and pressures, and upon the catalyst employed. For example when employing cobalt type catalyst, it is preferred to use about 1 mol of carbon monoxide to about 2 mols of hydrogen while when an iron catalyst is utilized, a mol ratio of 1/1 to 4/1 of hydrogen to carbon monoxide in the feed synthesis gases is desirable.

The synthesis gases comprising hydrogen and carbon monoxide are produced by various procedures. Methane or natural gas may be oxidized with a reducible metal oxide, with pure oxygen or with gases containing oxygen. Other feed stocks may comprise coal, shale and other hydrocarbons. The reaction may be conducted in a single or in a plurality of stages. When employing methane as feed gas and oxidizing the same with a reducible metal oxide, the reactions are generally conducted at temperatures in the range from about 1400° F. to about 2000° F. When the synthesis gases are produced, by utilizing oxygen and natural gas, the temperatures in the reaction zone are usually in the range from about 2000 to about 3000° F.

It is also known in the art to contact gases and solids by passing the gases upwardly through an enlarged treating zone, containing a body of finely-divided solids to be contacted, at a controlled velocity to maintain the solids in the treating zone in a quasi-liquid like state. Under properly controlled conditions, the subdivided solid particles are not only maintained in a highly turbulent, quasi-liquid and ebullient state, but there exists a rapid and overall circulation of the fluidized solids throughout the fluid bed.

Processes of this character, wherein fluidized solids are contacted with gases, have a number of inherent and important advantages. For example, intimate contact between the gases and the fluidized subdivided solids is secured. It is also possible to maintain a substantially uniform temperature throughout the bed as a result of the extremely rapid transfer of heat from one section of the bed to the other because of the rapid circulation of the fluidized subdivided solids. Furthermore, due to the rapid transfer of heat between the solids under these conditions, it is possible to readily add or extract heat from the mass at an extremely rapid rate. In fluidized operations, the solid subdivided particles generally have particle sizes in the range from about 0 to 200 microns and higher. These particles are maintained in a fluid ebullient state in the reaction zone by means of upflowing suspending gases, the velocity of which is in the range from about 0.1 to 5 feet and higher per second.

This invention finds specific application in a hydrocarbon synthesis reaction wherein the synthesis gases are reacted by means of a suitable catalyst to form hydrocarbon constituents containing more than one carbon atom in the molecule. For example, in this process one of the important problems confronting the development of the synthesis process is that carbon builds up on the catalyst to an extent that it is lost unless it is regenerated. Although a certain amount of carbon may be desirable on the catalyst surface, this factor must be controlled. As the carbon accumulates on the catalyst it disintegrates into finer particles. For example, catalyst containing no 0—20 micron material and 75% of 80+ micron fraction will be altered in 200 hours to 50% of 0—20 micron material and 10% of 80+ material. The finer material contained the most carbon, 50% as compared to 20% for the coarse particles. One main detrimental effect of carbon formation on the catalyst is the lower heat transfer property which results. This produces an attendant difficulty in maintaining satisfactory temperature control throughout the reactor bed. Thus, hot spots develop in the catalyst bed due to the poor heat transfer conditions. In accordance with this process, the character of the product gases and vapors is, therefore, able to be effectively controlled by controlling the carbon content of the catalyst in the treating zone.

In accordance with this invention, catalysts are employed which are less subject to attrition due to carbonization. By employing these catalysts, a more uniform product is secured for a longer period of time. These catalysts comprise hollow metal or metal oxide microspheres, the metal used being selected from the group consisting of iron, cobalt or nickel. These hollow microsphere catalysts may contain suitable promoters of the class enumerated heretofore. Particularly desirable promoters comprise potassium fluoride, sodium carbonate and/or potassium carbonate.

The hollow microspherical catalysts used in accordance with the present invention may conveniently be prepared by impinging a stream of molten metal of the group consisting of iron, cobalt and nickel on to the surface of a cooled, preferably curved, baffle whereby the stream of metal is broken into small particles which are then deflected downwardly away from the baffle into a cooling medium. The metal may be conveniently sprayed onto the surface of the baffle from a metal wire rod or equivalent by means of a metallizing gun. One convenient method of preparing the hollow metal spheres is illustrated in and by the single figure of the accompanying drawing.

Referring now to the drawing, iron wire (1) is introduced into metallizing gun (2). Fuel, as for example acetylene and oxygen, is supplied to the metallizing gun (2) by means of lines (3) and (4), respectively. The iron wire is projected through zone (A) and impinged against a curved baffle (10). For the purpose of description, the curved baffle is positioned approximately six feet from the nozzle of metallizing gun (2). Cooled water or an equivalent cooling medium is introduced into the interior of baffle (10) by means of line (5) and withdrawn from it by means of line (6). The temperature of the baffle (10) is maintained at substantially 200° F. The metal impinging upon the surface of baffle (10) is broken up into small particles, which particles fall downwardly through zone (B) and are collected in collecting means (20).

Any type of metallizing gun or equivalent means may be utilized. The particular metallizing gun used in conjunction with this work is a metallizing gun, designated by the trade name "Metco Metallizing Gun," (the word Metco being a Registered Trade Mark) manufactured by the Metallizing Engineering Company, Inc. of Long Island City, New York. The particular type of metal wire or rod employed should preferably be pure metal though carbon steels are very satisfactory.

The temperature in the zone between baffle and the metallizing gun is generally in the range from 2000° F. to 4000° F. In general, the baffle is positioned away from the gun so as to place the baffle in an oxidizing atmosphere. The molten metal should be impinged upon the baffle while hot whereby the metal is broken into particles having a micron size in the approximate range from 5 to 100 microns. The temperature on the surface of the baffle should preferably be in the range from 100 to 300° F., preferably at a temperature of substantially 200° F. It is believed that the temperature of the molten metal as it impinges upon the surface of the baffle is about 3000° F.

The process of this invention and the preparation of the catalyst may be readily understood by the following example illustrating the same.

EXAMPLE 1.

Iron wire was passed through a metallizing gun as described and impinged upon a curved baffle element. The baffle element was cooled and at a temperature of substantially 200° F. the resulting iron oxide spheres were collected and analyzed. The particle size distribution was as follows:

Micron Size	*Per Cent*
0—20	0.2
20—40	2.2
40—80	10.6
80—120	87

Prior to the analysis, slag was removed and the above particle size distribution of spheres represents approximately 90% recovery based upon the amount of iron wire used. The spheres were subjected to microscopic examination and to X-ray analysis which disclosed them to be hollow spheres and to be of a substantially crystalline structure of Fe_3O_4. The bulk density was 2.48.

From the above data it is apparent that a large recovery (90%) was made of the iron wire and that the resulting hollow microspheres have a substantially uniform particle size distribution in the range from substantially 80 to 120 microns. This is extremely desirable when it is necessary to manufacture catalyst particles for utilization in fluidized operations.

EXAMPLE 2.

Hollow iron oxide microsphere catalysts prepared as above and impregnated with 5% potassium fluoride, prepared in accordance with this process, were employed in various operations for the synthesis of hydrocarbons. The results of these operations are summarized as follows:

	Operation 1	*Operation* 2	*Operation* 3
Temperature, °F.	600	600	595
Feed, Hydrogen to CO ratio	1.08	1.1	1.16
Yields*	123	120	121

* cc. of hydrocarbons having four carbon atoms in the molecule and higher boiling constituent per cubic meter of hydrogen and carbon monoxide consumed.

EXAMPLE 3.

A catalyst comprising iron microspheres (oxidized 75%) and impregnated with 2½% of a potassium carbonate promoter was prepared as previously described. This catalyst was employed in a synthesis operation with the results as follows:

Temperature, °F.	600
Feed, H_2/CO Ratio	1.17
Gas Contraction, %	57
Yields, Collected:	
Hydrocarbons, cc./m. 3 H_2+CO Fed	131
H_2O, cc./m. 3 H_2+CO Fed	73

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is —

1. An improved hydrocarbon synthesis process which comprises introducing feed gases comprising carbon monoxide and hydrogen into a hydrocarbon synthesis reaction zone, maintaining temperature and pressure conditions in said reaction zone to secure the desired hydrocarbon synthesis reaction and contacting said feed gas in said reaction zone with hollow metal or metal oxide microsphere catalysts, the metal being selected from the group consisting of iron, cobalt or nickel.

2. A process according to Claim 1, wherein said microspheres have particle sizes in the range from substantially 0 to 200 microns and wherein said spheres are maintained in a fluid ebullient state in said reaction zone by means of an upflowing suspending gas.

3. A process according to Claim 1 or 2, wherein said metal comprises iron promoted with potassium fluoride.

4. A process according to Claim 1 or 2, wherein said metal comprises iron promoted with potassium carbonate.

5. A process according to any one of Claims 1—4, wherein the hollow metal microspherical catalysts are produced by impinging a stream of molten metal, e.g. from a spray gun or metallizing gun, on to a cooled preferably curved, baffle whereby the stream of metal is broken into small particles which are deflected downwardly away from said baffle into a cooling medium.

Dated this 14th day of August, 1947.

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Agents for the Applicants.

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