PATENT SPECIFICATION

727,833

Date of Application and filing Complete Specification Jan. 12, 1953.
No. 817/53.
Application made in United States of America on Jan. 17, 1952.
Complete Specification Published April 6, 1955.

Index at acceptance:—**Classes 1(1),** F3B1; **and 2(3),** B1G.

COMPLETE SPECIFICATION

Improvement in Hydrocarbon Synthesis

We, UNION CARBIDE AND CARBON CORPORATION, of 30, East 42nd Street, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignees of HUBERT GREENIDGE DAVIS jointly with THOMAS PUTNAM WILSON and ABRAHAM NATHAN KURTZ, all Citizens of the United States of America, of 228, Hayes Avenue, and 828, Bridge Road, Charleston, and Route 3, Box 348, St. Albans, State of West Virginia, United States of America, respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the synthesis of hydrocarbons from carbon monoxide and hydrogen whereby an increased yield of gaseous olefins is obtained.

It has been proposed to add chlorine or bromine or iodine or their hydrides or substances yielding either these halogens or their hydrides under the conditions of synthesis as inhibitors to an iron-base synthesis catalyst and to obtain redistributed hydrocarbon synthesis products which contain relatively increased amounts of gaseous olefins having from 2 to 4 carbon atoms. It has now been found that a further increase in the yield of these C_2—C_4 olefins is obtained when iron-base synthesis catalysts are subjected to a combined treatment with sulphur or sulphur compounds and the previously mentioned halogens or halogen compounds.

While sulphur alone has heretofore been used in the treatment of hydrocarbon synthesis catalyst, its effects have varied with the specific catalyst and method of treatment. Working with iron-base catalysis, we have determined that treatment of the catalysts with sulphur alone promotes the formation of saturated hydrocarbons of low molecular weight, in particular methane, ethane and propane. On the other hand, when sulphur is used to treat iron-base synthesis catalysts in combination with the halogens, chlorine, bromine, or iodine, or their hydrides or substances yielding either these halogens or their hydrides under the conditions of synthesis, an effect is obtained which is entirely different from that obtained when sulphur alone is used. The products formed in the presence of iron catalysts which have received this combined treatment contain a larger fraction of C_2—C_4 olefins than do the products produced by catalysts which have received only the halogen treatment. Also, the hydrocarbons formed from catalysts which have received the combined treatment contain only small amounts of C_2—C_4 paraffins, and the amount of methane produced is generally less than when sulphur alone is used to treat the catalyst.

According to this invention, the process for the synthesis of mixtures of hydrocarbons by passing a gaseous mixture containing carbon monoxide, hydrogen, and chlorine or bromine or iodine or their hydrides or substances yielding either these halogens or their hydrides under the conditions of synthesis, at a super-atmospheric pressure and at an elevated temperature over an iron-base catalyst is characterised in that the catalyst contains from 0.02% to 0.5% by weight of sulphur calculated as elemental sulphur. Treatment of the catalyst with sulphur may precede, accompany or follow the treatment with halogens. The treatment of the catalyst with halogen is effective for a relatively short duration because of chemical equilibrium considerations halogen is continuously evolved from the treated catalyst during the course of synthesis. Periodic or continuous replacement of the evolved halogen is necessary. On the other hand, the addition of sulphur to a halide-inhibited catalyst is effective for a longer period of time. However, in commercial practice, some replenishment of the sulphur content during the life of a commercial catalyst will undoubtedly be required. Because of the highly effective nature of the sulphur treatment, the sulphur may be added to the catalyst during preparation, in the form of an inorganic sulphate, for example, such as ferric or ferrous sulphate, but better control of the amounts to be added can be obtained by treating the catalyst *in situ* with synthesis gas containing a volatile compound of sulphur, such as diethyl sulphate, hydrogen sulphide, butyl or ethyl sulphide, ethyl or butyl mercaptan, carbon oxysulphide or carbon bisulphide.

The amount of sulphur to be added to the catalyst is quite important, as excessive additions of sulphur will destroy the catalyst activity. A noticeable increase in the amount of C_2—C_4 olefins formed is obtained when only 0.02% by weight of sulphur is added, calculated as elemental sulphur on the catalyst weight. The amount of these olefins formed increases up to a maximum value as the sulphur content of the catalyst is increased up to 0.10% by weight. Accompanying this increase in olefin content, obtained by increasing the concentration of sulphur on the catalyst, is a decline in the catalyst activity. An increase in the catalyst temperature is then necessary to maintain a constant rate of conversion of synthesis gas to total hydrocarbons. As a rough approximation, the reaction temperature should be raised 5° to 10° C. to maintain a constant rate of conversion of synthesis gas to hydrocarbons for each part of sulphur added per 10000 parts of catalyst, starting with unpromoted catalysts and an initial reaction temperature of 250 to 290° C. However, the conversion can be permitted to decline, and the reaction temperature raised less than this amount. Based on these considerations, the optimum sulphur content of the unpromoted catalyst is 0.04% to 0.1% by weight of the catalyst. Amounts of sulphur as high as 0.5% are the maximum amounts permissible with unpromoted iron catalysts.

Since both sulphur and halogens are added as inhibitors to the catalysts, the effects of sulphur must be considered in relation to the effects of halogen on the catalyst. As inhibition with halides also tends to decrease the activity of the catalyst careful correlation of the combined inhibition is necessary for the best results. Therefore, it is desirable to initiate the synthesis reaction with a reduced and well-activated catalyst and then bring the catalyst into a state of controlled and steady-state inhibition by treatment with sulphur and halogen inhibitors. It is preferable to add each type of inhibitor separately, although the order of addition of the inhibitors may be altered. Thus, after an initial treatment with halogen inhibitor, and when the halogen treatment has become stabilized and the characteristic effects of halogen inhibition obtained, which are an increase in the amount of the C_2—C_4 olefin fraction and a sharp increase in the ratio of water to carbon dioxide formed in the synthesis, then the treatment of the catalyst with sulphur may be commenced. By introducing the sulphur as a volatile compound with the synthesis gas, the amount of sulphur added to the catalyst can be carefully controlled and correlated with changes in the products of the reaction so that the optimum amount of sulphur will be added.

In order to demonstrate the difference in results obtained with the addition of halogen alone as an inhibitor and both halogen and sulphur as inhibitors, comparative runs were carried out. In each case, the catalyst was prepared from a taconite ore concentrate (Fe_3O_4) which had been roasted and ground to a size range of about 20 microns to 120 microns. Its particle size distribution was such that it was suitable as a fluid bed catalyst. The fluidized catalyst was reduced with hydrogen for 24 hours at 480° C. and atmospheric pressure with a flow rate of 250 to 400 cubic feet per hour per cubic foot of catalyst. The catalyst was then treated with synthesis gas (2.2 mols. H_2 : 1 mol CO) at 230 to 280° C. for four to six hours, the other conditions being the same as during the reducing period. Synthesis was then started at 60 lbs. per sq. in. gauge pressure using synthesis gas of the above composition and at the same linear velocity used in the forming process.

In both runs, halogen inhibition was instituted by feed beta,beta^1-dichlorethyl ether into the synthesis gas in an amount equal to the equilibrium concentration. An equilibrium concentration of inhibitor is that concentration at which the calculated pressure of HCl resulting from complete decomposition of the chlorinated ether equals the equilibrium pressure of HCl for the Fe—FeO—H_2—HCl system under the conditions existing at the outlet end of the catalyst bed. In one of these runs, ethyl sulphate corresponding to 0.05% sulphur by weight of the catalyst was then added over a period of one hour by saturating the entering synthesis gas with the volatile sulphate. Inhibition of the catalyst with dichlorethyl ether was continued during and after the inhibition with sulphur.

The results of the runs are given in the table below:—

TABLE

EFFECTS OF SULPHUR AND HALIDE INHIBITION

Run No.	1		2	
Inhibitor	chloride alone		sulphur plus chloride	
Temp. ° C.	328		372	
Pressure, (gauge) lbs./sq. in.	60		60	
Inlet space velocity*	1600		1600	
Conversion, %	39		36	
Age of catalyst, hrs.	180		330	
Sulphur added, % by weight of catalyst	None		0.05	
Products, % of total hydrocarbons, carbon atom basis				
CH_4		9		23
C_2H_6	1.6		3.1	
C_3H_8	0.8		0.7	
C_4H_{10}	0.5		0.4	
C_2—C_4 paraffins		2.9		4.2
C_2H_4	9.3		21.5	
C_3H_6	16.6		22.2	
C_4H_8	10.2		10.8	
C_2—C_4 olefins		36.1		54.5
C_5 + (estimated)		48		15
Undetermined		4		3
Total		100		99.7
Run No.	1		2	
$CO_2/(CO_2+H_2O)$, %	3		6	

*Cubic feet per hour per cubic foot of catalyst

From these results it is seen that treatment of the catalyst with halogen alone promotes the formation of C_2—C_4 olefins, but considerable amounts of heavier fractions are also obtained. The combined inhibition with sulphur and chlorine has a very specific effect giving a high yield of the desired C_2—C_4 olefins. Most significantly, there is practicaly no increase in the amount of C_2—C_4 paraffins formed resulting from the combined treatment of the catalyst with sulphur and chlorine, but there is a very appreciable increase in the amount of C_2—C_4 olefins formed. Also, the combined treatment with sulphur and chlorine causes a redistribution of the olefins in the C_2—C_4 fraction, over that resulting from chlorine inhibition alone, in particular the yield of ethylene being more than doubled.

With respect to the effect of the combined inhibition on the other reaction conditions, it is seen that the reaction temperature has been increased in order to maintain a good conversion of synthesis gas to total hydrocarbons. Also, it is noted that water is the principal co-product of the synthesis when halogen is used alone or in combination with sulphur. The formation of water as the co-product of the synthesis is advantageous as it is easier to remove from the other gases.

The temperature of the reaction may be in the range of 250° to 420° C., and preferably in the range of 300° to 380° C. The reaction pressure may vary from 25 to 500 lbs. per sq. in. absolute, but is preferably within the range of 60 to 300 lbs. per sq. in. absolute. Also, the synthesis gas ratio, H_2 mols: CO mols, may vary from 1 : 2 to 5 : 1.

What we claim is:—

1. A process for the synthesis of mixtures of hydrocarbons by passing a gaseous mixture containing carbon monoxide hydrogen, and chlorine or bromine or iodine or their hydrides or substances yielding either these halogens or their hydrides under the conditions of synthesis, at a superatmospheric pressure and at an elevated temperature over an iron-base catalyst, characterized in that the catalyst contains from 0.02% to 0.5% by weight of sulphur calculated as elemental sulphur.

2. A process as claimed in claim 1 in which the sulphur content of the catalyst is from 0.04% to 0.1% by weight.

3. A process as claimed in claim 1 or 2, in which the elevated temperature is within the range of 250° C. to 420° C.

4. A process as claimed in any one of the preceding claims in which the superatmospheric pressure is from 25 to 500 lbs. per sq. in. absolute.

5. A process as claimed in any one of the preceding claims in which the sulphur is present in the catalyst in the form of an inorganic sulphate.

6. A process as claimed in claim 5, in which the sulphur is present as ferric or ferrous sulphate.

7. A process as claimed in any one of claims 1 to 4, in which a volatile sulphur compound is introduced into the synthesis gas.

8. A process as claimed in claim 7, in which the volatile sulphur compound is diethyl sulphate.

9. A process for the synthesis of mixtures of hydrocarbons having a relatively high concentration of normally gaseous olefins containing from 2 to 4 carbon atoms, by passing a gaseous mixture containing carbon monoxide and hydrogen at superatmospheric pressure and at an elevated temperature over an iron-base catalyst as hereinbefore particularly described in connection with Run 2 of Table 1.

10. Mixtures of synthetic hydrocarbons having a relatively high concentration of normally gaseous olefins containing from 2 to 4 carbon atoms whenever prepared by the process as hereinbefore particularly described and claimed in any one of the preceding claims.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patent Act, 1949 to Patent No. 692,158.

**Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.**