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(54) HYDROCARBON SYNTHESIS

(54) SYNTHÈSE D'HYDROCARBURE

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3.

1 carbon synthesis process which produced the same constituents as natural gas, would be of little economic value at present, even though the synthetic gas was richer in the higher paraffins.

On the other hand, when sulfur is used to treat iron-base synthesis catalysts in combination with the halogens, chlorine, bromine, or iodine, or compounds of these halogens, an effect is obtained which is entirely different from that obtained when sulfur alone is used.

10 The products formed in the presence of iron catalysts which have received this combined treatment contain a larger fraction of C₂-C₄ 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 C₂-C₄ paraffins, and the amount of methane produced is generally less than when sulfur alone is used to treat the catalyst.

Treatment of the catalyst with the halogens is
20 carried out as described in U.S. Patent No. 2,717,259, to H.G.Davis and T.P.Wilson, and treatment of the catalyst with sulfur may precede, accompany or follow the treatment with halogens. As pointed out in that patent, the treatment with halogens is not permanent and halogen is lost from the halided catalyst during the course of synthesis because of equilibrium considerations which necessitates periodic or continuous replacement of the depleted halogen. On the other hand, the effect of adding sulfur to a halide-inhibited catalyst
30 is much more permanent and the effects of a single treat-

1 ment persist over runs of considerable duration. However,
in commercial practice, some replenishment of the sulfur
content during the life of a commercial catalyst will
undoubtedly be required. Because of the relatively per-
manent nature of the sulfur treatment, the sulfur may be
added to the catalyst during preparation, in the form of
an inorganic sulfate, for example, such as ferric or
ferrous sulfate, but better control of the amounts to be
10 added can be obtained by treating the catalyst in situ
with synthesis gas containing a volatile compound of sul-
fur, such as diethyl sulfate, hydrogen sulfide, butyl or
ethyl sulfide, ethyl or butyl mercaptan, carbon oxysulfide
or carbon bisulfide.

The amount of sulfur to be added to the cata-
lyst is quite important, as excessive additions of sulfur
will destroy the catalyst activity. A noticeable increase
in the C₂-C₄ olefins formed is obtained when only 0.02% by
weight of sulfur is added, calculated as elemental sulfur
on the catalyst weight, and the amounts of these olefins
20 formed increase up to their maximum values as the sulfur
content of the catalyst is increased up to 0.10% by weight.
Accompanying this increase in olefin content with increas-
ing concentration of sulfur on the catalyst is a decline
in the catalyst activity, necessitating an increase in
the catalyst temperature to maintain a constant conversion
of synthesis gas to total hydrocarbons. As a rough ap-
proximation, the reaction temperature should be raised
5° to 10°C. to maintain constant conversion for each part
of sulfur added per 10,000 parts of catalyst, starting
30 with unpromoted catalysts and an initial reaction tem-

560816

1 perature 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 sulfur content of the unpromoted catalysts
is 0.04 to 0.1% by weight of the catalyst. Amounts of
sulfur as high as 0.5% are the maximum amounts permissible
with unpromoted iron catalysts. By the addition of alkali
promoters, however, the tolerance of the catalyst for
sulfur can be increased.

10 Since both sulfur and halogens are added as in-
hibitors to the catalysts, the effects of sulfur must be
considered in relation to the effects of halogen on the
catalyst. As inhibition with halides also tends to de-
crease the activity of the catalyst, careful correlation
of the combined inhibition is necessary for the best re-
sults. Therefore, it is desirable to initiate the syn-
thesis 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 sulfur and
20 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 in-
crease in the C₂-C₄ 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 sulfur
may be commenced. By introducing the sulfur as a volatile
30 compound with the synthesis gas, the amount of sulfur

1 added to the catalyst can be carefully controlled and correlated with changes in the products of the reaction so that the optimum amount of sulfur will be added.

10 In order to demonstrate the difference in results obtained with the addition of halogen alone as an inhibitor and both halogen and sulfur 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 H_2 :1CO) at 230 - 280°C. for four to six hours, the other conditions being the same as during the reducing period. Synthesis was then started at 60 psig. using synthesis gas of the above composition and at the same linear velocity used in the forming process.

20 In both runs, halogen inhibition was instituted by feeding beta,beta'-dichlorethyl ether with the synthesis gas at equilibrium conditions. 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-FeO₂-H₂-HCl system under the conditions existing at the outlet end of the catalyst bed. This equilibrium concentration is further described in the above-mentioned application, Serial No.

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1 136,813. In one of these runs, ethyl sulfate corresponding to 0.05% sulfur by weight of the catalyst was then added over a period of one hour by saturating the entering synthesis gas with the volatile sulfate. Inhibition of the catalyst with dichlorethyl ether was continued during and after the inhibition with sulfur.

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

TABLE I

EFFECTS OF SULFUR AND HALIDE INHIBITION

Run No.	1	2
In hibitor	Chloride alone	Sulfur plus chloride
Temp. °C.	328	372
Pressure psig.	60	60
10 Inlet space velocity CFH gas/CF Cat.	1600	1600
Conversion, %	39	36
Age of catalyst, Hrs.	180	330
Sulfur added, % by weight of catalyst	None	0.05
Products, % of total hydrocarbons, carbon atom basis		
CH ₄	9	23
C ₂ H ₆	1.6	3.1
C ₃ H ₈	0.8	0.7
20 C ₄ H ₁₀	0.5	0.4
C ₂ -C ₄ paraffins	3	4
C ₂ H ₄	9.3	21.5
C ₃ H ₆	16.6	22.2
C ₄ H ₈	10.2	10.8
C ₂ -C ₄ olefins	36	55
C ₅ + (Estimated)	48	15
Undetermined	4	3
Total	100	100
CO ₂ /(CO ₂ +H ₂ O), %	3	6

30 From these results it is seen that treatment
of the catalyst with halogen alone promotes the formation

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1 of C₂-C₄ olefins, but considerable amounts of heavier
fractions are also obtained. The combined inhibition
with sulfur and chloride has a very specific effect giving
a high yield of the desired C₂-C₄ olefins. Most signifi-
cantly, there is practically no increase in the C₂-C₄
paraffins resulting from the combined treatment of the
catalyst with sulfur and chlorine, but there is a very
appreciable increase in the amount of C₂-C₄ olefins formed.
Also, the combined treatment with sulfur and chlorine
10 causes a redistribution of the olefins in the C₂-C₄ frac-
tion, 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 in-
hibition on the other reaction conditions, it is seen that
the reaction temperature has been increased in order to
maintain the conversion of synthesis gas to total hydro-
carbons. Also, it is noted that water is the principal
co-product of the synthesis when halogen is used alone or
in combination with sulfur. The formation of water as the
20 co-product of the synthesis is advantageous as it is easier
to remove from the other gases.

In so far as the other conditions of the reaction
are concerned, they do not differ radically from that
described in U. S. Patent No. 2,717,259. Thus, the
temperature of the reaction may be in the range of 250°C.
to 420°C., and preferably in the range of 300°C. to
380°C. The reaction pressure may vary from 25 to 500 psi.
absolute, but is preferably within the range of 60 to 300
psi. absolute. Also, the synthesis gas ratio, H₂:CO, may
30 vary from 1:2 to 5:1. The inhibition with halides is also

1 carried out as described in the above application, and
consists in subjecting the catalyst during synthesis to
intimate contact with regulated amounts of members of the
groups consisting of (1) chlorine, bromine and iodine, (2)
hydrogen chloride, hydrogen bromide and hydrogen iodide,
and (3) halide-containing compounds capable of releasing
the aforesaid halogens or halogen halides in contact with
the catalyst.

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1 The embodiments of the invention in which an
exclusive property or privilege is claimed are defined
as follows:

10 1. In the process for making hydrocarbons by
the reaction of carbon monoxide and hydrogen in the pres-
ence of an iron-base catalyst, the improvements which
comprise incorporating a small amount of sulfur in the
catalyst and subjecting the catalyst during the reaction
to intimate contact with regulated amounts of members of
the group consisting of (1) chlorine, bromine and iodine,
(2) hydrogen chloride, hydrogen bromide and hydrogen iodide
and (3) halide-containing compounds capable of releasing
the aforesaid halogens or halogen halides in contact with
the catalyst.

 2. Process as claimed in claim 1 in which the
amount of sulfur is from 0.02 to 0.5% by weight of the
catalyst.

20 3. Process as claimed in claim 2 in which the
amount of sulfur is from 0.04 to 0.1% by weight of the
catalyst.

 4. Process of making hydrocarbons containing a
substantial amount of olefins having from two to four car-
bon atoms which comprises passing a mixture containing
carbon monoxide and hydrogen under super-atmospheric pres-
sure over an iron-base catalyst containing a small amount
of sulfur at a temperature of 250° to 420°C., and subject-
ing the catalyst during the reaction to intimate contact
30 with regulated amounts of members of the group consisting

1 of (1) chlorine, bromine and iodine, (2) hydrogen chloride, hydrogen bromide and hydrogen iodide and (3) halide-containing compounds capable of releasing the aforesaid halogens or halogen halides in contact with the catalyst.

10 5. Process of making hydrocarbons containing a substantial amount of olefins having from two to four carbon atoms which comprises passing a mixture containing carbon monoxide and hydrogen under super-atmospheric pressure over an iron-base catalyst at a temperature of 250° to 420°C., and subjecting the catalyst during the reaction to intimate contact with controlled amounts of a volatile sulfur compound and with regulated amounts of members of the group consisting of (1) chlorine, bromine and iodine, (2) hydrogen chloride, hydrogen bromide and hydrogen iodide and (3) halide-containing compounds capable of releasing the aforesaid halogens or halogen halides in contact with the catalyst.

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