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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Hydrocarbon Synthesis

We, 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 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 relates to improvements in the reduction of the oxides of carbon to form normally liquid hydrocarbons and oxygenated hydrocarbons. More particularly the present invention relates to improvements in the production of the said normally liquid hydrocarbons and oxygenated hydrocarbons in the presence of a fluidized bed of finely divided iron catalyst.

Heretofore and prior to the present invention, it was known that hydrocarbons boiling in the gasoline boiling range and heavy hydrocarbons could be synthesized by reacting the oxides of carbon with hydrogen in the presence of a suitable catalyst. The original work in this field was performed in the presence of cobalt, utilizing a fixed bed of such catalyst. For instance, a feed gas containing 2 mols. of hydrogen per mol. of carbon monoxide was charged to a reactor containing metallic cobalt carried on a support, usually kieselguhr, and the catalyst composition also included a promoter which was ordinarily, thoria. The operation was conducted at a temperature within the range from about 325°—450° F. and was operated under pressures, which were atmospheric or superatmospheric. The product obtained was for the most part straight chain paraffinic with respect to the hydrocarbon product. Minor amounts of alcohols, aldehydes and other hydrogenated compounds were also formed.

Thereafter further research developed a modification of the foregoing process wherein the reaction was carried out at somewhat higher pressures and in the presence of an iron catalyst. This process also differed from the earlier process in that the temperatures employed were somewhat higher, namely, within the general range of 550°—700° F. or higher. This latter process was further differentiated from the older cobalt process in that the mol ratio of hydrogen to carbon monoxide in the feed to the reaction zone was less than 2:1, and that it is varied from a 1:1 to a 1.8:1 hydrogen to carbon monoxide ratio in the fresh feed. The product obtained in this process was of different character from that employed in the earlier process in that it was less saturated and consequently, the gasoline fraction was of better quality.

Still more recently the hydrocarbon synthesis process has engaged the attention of technologists who have attempted to apply the fluidized catalyst type of operation to the said synthesis. Indeed, at the present time, considerable research is being carried out in this country directed toward synthesizing gasoline from hydrogen and carbon monoxide in a process in which a promoted fluidized iron catalyst is contacted with feed gas under conditions of elevated temperatures and pressures in order to form in a single step (with and without recycle of unconverted feed) gasoline of good octane rating. It is very desirable to perfect such a process for, of course, the hydrocarbon synthesis reaction is highly exothermic and in the older fixed bed type of operation temperature control constituted a very serious and difficult problem. It is one of the attributes of fluidized catalyst technique, that the turbulent state of the catalyst is conducive to thorough mixing of all portions thereof, and with it, a positive tendency to cause uniformity of temperature throughout the bed of fluidized catalyst.

[Price 2/8]

Although the art has had some experience in the commercial practice of fluid catalyst technique, as for instance in catalytic cracking of hydrocarbon oil, the attempt to apply this technique to hydrocarbon synthesis has revealed a large number of problems not encountered in catalytic cracking. This, of course, is understandable for many reasons, including the fact that the catalytic cracking of hydrocarbon oil is an endothermic reaction while hydrocarbon synthesis is a highly exothermic reaction and the further fact that the hydrocarbon synthesis reaction unavoidably results in the deposition of substantially more carbonaceous material on the catalyst, which depositions are closely connected with physical disintegration of the catalyst to particle sizes which are not adapted for good fluidization, because of their extreme fineness. The foregoing specifically mentioned problems and numerous others have confronted the researchers who have striven to adapt the fluid catalyst technique to hydrocarbon synthesis in the laboratories, in pilot plants and in semi-commercial operations and it is an object of this invention to alleviate these insufficiencies of operation which have thus been encountered, all of which will more fully appear hereinafter in the present specification.

One of the problems involved in applying fluid catalyst technique to hydrocarbon synthesis has to do with maintaining the catalyst at a high level of activity. For example, although reduced iron is charged to the reactor during the course of the reaction, there is a tendency for the catalyst to become oxidized by the water vapor and/or carbon dioxide present in, or formed in the reduction of carbon monoxide to form hydrocarbons. It can be assumed that the reaction will proceed according to one or both of the equilibrium reactions below:—

$$CO+2H_2 \rightleftarrows CH_2+H_2O$$

$$2CO+H_2 \rightleftarrows CH_2+CO_2$$

In any event it is obvious that the oxygen of the carbon monoxide must be eliminated and it is equally obvious that either water or carbon dioxide or probably both will be formed in the reaction zone. Under the conditions prevailing in the reaction zone, the water and/or the carbon dioxide tend to oxidise the catalyst. Experience has shown that if the catalyst contains 20 weight % or more oxygen, it is less active than catalyst containing a lower percentage of oxygen. Furthermore, synthesis catalysts containing a relatively high oxygen content tend to deposit excessive quantities of wax on the catalyst at synthesis conditions. This deposition of wax adversely affects the fluidization characteristics of the catalyst. Now since carbon dioxide and water are unavoidably formed in the reaction, it would be desirable to prepare a catalyst which will resist oxidation by these constituents of the gasiform reaction mixture, since the activity and selectivity of the catalyst will thereby be maintained at a high level.

Another equally serious problem in the fluid-type iron-catalyzed hydrocarbon synthesis is presented by the strong tendency of the catalysts to disintegrate in the course of fluid operation apparently as a result of excessive deposition of free carbon on the catalyst. This carbonization and disintegration tendency of fluidized iron catalysts has been combated more recently with considerable success by a so-called precarbiding treatment of the catalyst in which the catalyst is subjected to the influence of CO-containing gases, such as mixtures containing H_2 and CO in the ratio of 2—8 : 1, at atmospheric to about 600 lbs. per sq. in. pressure and temperatures of about 500°—1100° F. until a desired amount of carbon, say about 0.5—5 wt. %, was incorporated in the catalyst as iron carbide. However, this precarbiding treatment has merely a surface effect and the carbide disappears fairly rapidly from the catalyst surface at synthesis conditions particularly when high H_2 proportions are present in the total (fresh + recycle) feed. Therefore, the carbiding treatment, in order to exert its beneficial effects throughout runs of several hundred hours had to be repeated at frequent intervals. A precarbided iron catalyst which will retain its carbide content under synthesis conditions for a longer period of time, therefore, is a need strongly felt in the synthesis art.

It is an object of the present invention to prepare a powdered iron catalyst which is relatively resistant to oxidation in a hydrocarbon synthesis reaction zone and which when precarbided will retain its carbide content for a satisfactory length of time under synthesis conditions.

It is also an object of the invention to prepare a catalyst which will not form excessive deposits of wax during the hydrocarbon synthesis reaction, and thus improve its fluidization characteristics.

In accordance with the invention a powdered iron catalyst is prepared by subjecting fresh (as opposed to regenerated) iron oxide to a reducing treatment with hydrogen at a temperature within the range of 900—1500° F. and subjecting the thus reduced catalyst, before use in the hydrocarbon synthesis reaction, to an activating or precarbiding treatment with a mixture containing hydrogen and carbon monoxide in the proportion of 2—8 molecules of hydrogen per molecule of carbon monoxide at a temperature between 500° and 700° F. The second step of treating the reduced catalyst with a mixture of CO and H_2 is preferably a precarbiding operation carried out so that 50—55% by weight of the iron is converted into iron carbide. A further feature of the invention involves a second catalyst reducing treatment with hydrogen at a temperature between 500° and 700° F. following the initial high temperature reducing treatment and preceding the treatment with carbon monoxide and hydrogen. As will be shown subsequently herein, a catalyst thus prepared is relatively stable toward oxidation during the hydrocarbon synthesis process thus maintaining good selectivity to useful products, and also retains carbide carbon incorporated by precarbiding for a considerably longer time under synthesis conditions than catalyst which is merely reduced by conventional low temperature hydrogen treatment. In the synthesis step, gas mixtures of hydrogen and carbon monoxide are employed wherein the mol. ratio of hydrogen to carbon monoxide is less than 2.

In order to give full details and a preferred modification of the invention it is pointed out that powdered iron oxide having a particle size of from 0—200 microns and containing particles having a size greater than 80 microns to the extent of 50% or more, is impregnated with a suitable promoter such as potassium fluoride, sodium carbonate, potassium chloride and potassium carbonate, and then subjected to a temperature within the range of 900°—1500° F., preferably 1000°—1100° F. in an atmosphere of substantially hydrogen until the oxygen content of the iron is reduced preferably to a value within the limits of from about 3—10 weight per cent. Thereafter, the catalyst is further treated at a temperature within the range of 500°—700° F. for a period of several hours with a mixture of hydrogen and carbon monoxide in the proportions indicated.

Tests have shown that samples of iron oxide, specifically pyrites ash containing sodium carbonate, reduced and treated under the conditions set forth above were much less susceptible to oxidation by H_2O and CO_2 and retained iron carbide much longer than samples of the same material hydrogen-treated exclusively at temperatures within the range of from 700°—900° F. which is the usual reduction temperature for iron catalysts.

There are set forth below in tabular form the results of tests carried out using a pyrites ash catalyst impregnated in one case with ½ weight per cent. of sodium carbonate (based on the iron) and in the other with 1% by weight of potassium chloride. As appears from the tabulation, at the left hand column, the temperature conditions employed for complete reduction prior to oxidation are set forth. In the 2nd, 3rd, and 4th columns under the general heading "Conditions Employed For Oxidation Treatment," the treating gas, the temperature of the treatment and the duration thereof are set forth and then in the 5th and 6th columns there is set forth the increase in weight per cent. oxygen acquired by the iron exposed to the oxidizing effect of steam and carbon dioxide under temperature conditions comparable to those employed in the hydrocarbon synthesis zone.

TABLE A

Catalyst: Iron pyrites ash plus 1/2% Na_2CO_3 or 1% KCl Employed

Conditions for Complete Reductions Prior to Oxidation Treatment	Conditions Employed for Oxidation Treatment			Increase in Weight % Oxygen	
Temp., °F.	Gas	Temp., °F.	Hours	Na_2CO_3 Promoted	KCl Promoted
700	H_2O+N_2	550	4	16.5	
1100	H_2O+N_2	550	4	9.2	
700	H_2O+N_2	700	4	16.9	
900	H_2O+N_2	700	4	17.5	15.2
1100	H_2O+N_2	700	4		11.0
1200	H_2O+N_2	700	4	10.9	
900	Dry CO_2	700	4	15.9	16.8
1100	Dry CO_2	700	4		7.2
1200	Dry CO_2	700	4	7.4	

It can be seen from the foregoing data that as the temperature employed for the reduction of the catalysts was increased, the extent of oxidation decreased during the subsequent oxidation tests. This is true for oxidation by both water vapor and CO_2.

The beneficial influence of the high temperature hydrogen treatment on pre-carbiding and carbide retention of iron catalysts is demonstrated hereinafter by further experimental data.

Two samples of ammonia synthesis catalysts which is a fused magnetite, containing among other ingredients as is known, potassia and a substantial amount of alumina were reduced at 700° F. in the conventional manner and at 1100° F. in accordance with the invention respectively. Thereafter different batches of these catalysts were subjected to pre-carbiding treatments with gas mixtures containing H_2 and CO in the ratio 8:1 or 2:1 for different times. The essential conditions and results of these tests are tabulated in Table B below:

TABLE B

H_2 + CO Treatment At 700° F. And 120 V/Hr./W		Analysis After Treatment, Wt. %					
		700° F. Reduction			1100° F. Reduction		
H_2/CO	Time, Hrs.	Total Carbon	Carbide Carbon	Wt. % of Fe Carbided	Total Carbon	Carbide Carbon	Wt. % of Fe Carbided
8/1	0.25	5.2	3.0	35	6.4	3.8	43
”	0.50	9.4	3.5	41	7.5	4.2	48
”	1.0	13.2	3.2	39	10.1	4.6	54
2/1	0.50	18.1	3.3	43	14.4	4.2	53
”	1.0	24.9	3.0	44	21.2	3.7	50

It will be observed that carbiding was effected to a greater extent on the catalyst reduced at 1100° F. than on the catalyst reduced at 700° F. (50—55 vs. 40—45% of Fe carbided).

It is also shown by the above data that carbon formation (Total Carbon “ minus ” Carbide Carbon) is less on the material reduced at the elevated temperature (1100° F.).

Further experimental work was carried ou using three different catalysts of the following composition:

	Wt. % on Ash Basis		
Constituent	Ammonia Synthesis Catalyst	Pyrites Ash Catalyst May, 1946	Mill Scale Catalyst
Fe_2O_3	93.62	95.88	97.0
SiO_2	1.33	1.48	0.5
Al_2O_3	2.5	0.40	*
MnO	0.79	0.11	0.4
CuO	0.10	0.13	*
MgO	0.11	0.71	*
ZnO	—	0.25	*
CaO	Trace	0.85	*
MoO	—	—	
Cr_2O_3	Trace	0.04	0.1
NiO	0.05	0.06	
K_2O	1.50	—	0.7
S	—	0.09	—
Total	100.00	100.00	98.7

X-Ray Analysis indicates that in the Ammonia Synthesis Catalyst the iron is for the most part in the form of Fe_3O_4; in the case of Pyrites Ash it is in the form of Fe_3O_4 and Fe_2O_3 for the most part; while in the case of Mill Scale Catalyst the iron is for the most part in the form of FeO.

* Indicated to be present by qualitative spectrographic analysis.

Different samples of these three catalysts were hydrogen treated at 700° F. and 1100° F. respectively and tested for oxidation tendency and carbide retention substantially as described above. The essential test conditions and the results obtained are tabulated and discussed below.

Effect of Temperature of Reduction on Oxidation Tendency.

Samples of the various catalysts were reduced at 700° F. (16 to 24 hours) and at 1100° F. (1½ to 2 hours) employing electrolytic hydrogen at atmospheric pressure and then treated at 600° F. for 4 hours at atmospheric pressure with nitrogen containing 4 mol. % H_2O and at 400 psig. with $2/1H_2/CO$.

Table C

Wt. % O_2 After Treating (C—+O— free basis)

Catalyst	Sample Reduced at 700° F.		Sample Reduced at 1100° F.	
	N_2+H_2O	2/1 Gas	N_2+H_2O	2/1 Gas
Mill Scale	6.4	5.9	4.4	2.4
Pyrites Ash	20.7	17.8	9.1	12.7
Ammonia Synthesis Catalyst (LCSA #3)	22.7	23.8	12.9	19.6

It is manifest from these data that the oxidation tendency of the catalysts of the invention is substantially less than that of conventionally reduced catalysts.

Effect of Temperature of Reduction and Subsequent Carbiding on Oxidation Tendency and Carbide Retention

Laboratory tests were made to determine the effect of temperature of reduction and subsequent carbiding on the oxidation tendency and to determine the effect of temperature of reduction on carbide retention. The averaged data showing the effect of reduction plus carbiding, as compared with reduction alone, on the oxidation tendency (N_2+4 mol. % of H_2O) of the three different catalysts are summarized in the following tabulation.

Table D

Oxygen Content After Treat. Wt. % (C— and O— Free Basis)

Catalyst	Reduced Catalyst		Reduced and Carbided Cat.	
	700° F. Red'n	1100° F. Red'n	700° F. Red'n	1100° F. Red'n
Mill Scale	6.4	4.4	4.4	2.7
Pyrites Ash	20.7	9.1	11.7	5.8
Amm. Syn. Catalyst	22.7	12.9	15.8	9.2

These data show the following:

1. Carbided, reduced catalysts are more resistant to oxidation than uncarbided, reduced catalysts.

2. For carbided catalysts, as for uncarbided catalysts, reduction at 1100° F. is superior to reduction at 700° F. in rendering the catalysts more resistant to oxidation.

Data showing the effect of temperature of reduction on carbide retention for these three catalysts are summarized in the following tabulation:

Table E

Wt. % Fe Carbided (Calculated as Fe C) After N_2+H_2O Test (4 Hours)

Catalyst	700° F. Reduction		1100° F. Reduction	
	Before Treat	After Treat	Before Treat	After Treat
Mill Scale	47	42	39	37
Pyrites Ash	44	29	43	40
Amm. Syn. Catalyst	39	19	41	28

These data obtained by oxidation with $N_2 + 4$ mol. % H_2O at atmospheric pressure show the following:

1. Mill scale reduced at 1100° F. and at 700° F. showed little or no loss of carbide.

2. Coke resintered pyrites ash reduced at 1100° F. showed practically no change in carbide content, but the samples reduced at 700° F. showed a considerable loss of carbide.

3. Ammonia synthesis catalyst reduced at 1100° F. and at 700° F. showed an appreciable loss of carbide; the loss was greater however, for the catalyst reduced at 700° F.

Analyses made after treating the reduced, carbided catalysts for 4 hours with 2/1 H_2/CO at 400 psig, showing the effect of temperature of reduction plus carbiding, as compared with temperature of reduction alone, on the oxidation tendency of three different catalysts are summarized below:

TABLE F

Oxygen Content After Treat. Wt. % (C— and O— Free Basis)

Catalyst	Reduced Catalyst		Reduced and Carbided Cat.	
	700° F. Red'n	1100° F. Red'n	700° F. Red'n	1100° F. Red'n
Mill Scale	5.9	2.4	4.1	2.2
Pyrites Ash	17.8	12.7	7.8	6.7
Amm. Syn. Catalyst	23.8	19.6	22.8	11.7

These data are comparable to and generally corroborate the results by oxidation with $N_2 + 4$ mol % of H_2O at atmospheric pressure, and show that both carbiding and high temperature of reduction increase the resistance of the catalysts toward oxidation.

Data showing the effect of temperature of reduction on carbide retention under hydrocarbon synthesis conditions for these three catalysts are summarized below:

TABLE G

Wt. % Fe Carbided (Calculated as Fe_2C)

Catalyst	700° F. Reduction		1100° F. Reduction	
	Before Treat	After Treat	Before Treat	After Treat
Mill Scale	47	44	39	44
Pyrites Ash	44	42	43	40
Amm. Syn. Catalyst	39	10	41	26

These data show the following:

1. Mill scale and coke resintered pyrites ash catalysts reduced at 1100° F. and at 700° F. showed little change in loss of carbide content.

2. Ammonia synthesis catalyst reduced at 1100° F. and at 700° F. showed an appreciable loss of carbide; the loss was greater for the catalyst reduced at 700° F. than for the catalyst reduced at 1100° F.

The results of pilot unit operation on pyrites ash initially reduced at 1050° F. and 700—750° F., respectively, are given in Table H.

TABLE H

HYDROCARBON SYNTHESIS FLUID UNIT

400 Psig., 650° F.

Run No.	69*		61**
Catalyst	— Pyrites Ash —		
Hours	20—115	157—180	10—117
H_2/CO,F.F.	1.85		2.06
Recycle/F.F.	1.95		1.8
Total Feed			
H_2P.P.	180		205
H_2/H_2+C	0.64		0.70
V/Hr./W	39		39
% Conversion of Feed			
CO	99.1	98.4	98.8
H_2+CO	95.3	98.1	92.3
cc./m^3 H_2+CO Consumed			
C_3+	245	245	230
C_4+	193	194	180
EtOH	33	37	30
C_1+C_2, Predicted	21.6	19.9	24.4
C_1+C_2, Actual	16.5	14.7	19.5

The excellent activity and superior liquid product selectivity of the catalyst of Run No. 69 are manifest. The catalyst of Run No. 69 was discharged in good condition after 388 hours of operation.

*Reduced at 1050° F.

**Reduced at 700°—750° F. and precarbided.

The beneficial effect of hydrogen treatment in accordance with the present invention, on catalyst disintegration tendencies under conditions essentially simulating those of fluid type synthesis operation is further borne out by the specific disintegration test data given in Table I below. All essential disintegration test conditions are listed in the heading of the table. The meaning of the definition used to characterize the catalyst preparation is explained in the foot notes of the table.

TABLE I

FLUID CATALYST DISINTEGRATION TESTS
EFFECT OF TEMPERATURE OF REDUCTION ON CATALYST DISINTEGRATION
ATMOSPHERIC PRESSURE GLASS UNIT

Temp: 700° F.; Feed: 2/1 H_2/CO Scrubbed; Gas Vel: 0.7—0.8 Ft./Sec.

Catalyst	— Pyrites Ash —				— Mill Scale —	
Promoter	— 1.5% K_2CO_3 —				— Ca 0.5% K_2O —	
Reduction Temperature, °F.	700	900	1050	1200	700	900

TABLE I.—*cont.*

FLUID CATALYST DISINTEGRATION TESTS
EFFECT OF TEMPERATURE OF REDUCTION ON CATALYST DISINTEGRATION
ATMOSPHERIC PRESSURE GLASS UNIT.

Temp: 700° F.; Feed: 2/1 H_2/CO Scrubbed; Gas Vel: 0.7—0.8 Ft./sec.

Disintegration						
Run No.	1	2	3	4	5	6
Run Length, Hours	7	7	7	34.5	7	21
Charge						
Oxygen, % (a)	0.3	2.3	1.4	1.5	0.9	0.6
Roller, 0—20 Microns	0	0	0	1	1	0
20—40 ,,	2	1	0	15	9	3
40—80 ,,	45	13	18	25	46	54
80+ ,,	53	86	82	59	44	43
Discharge						
Oxygen, % (a)	0.1	0.0	1.2	1.0	1.1	0.0
Carbon, % Determined (a)	27.5	23.1	21.5	23.3	32.3	25.0
Carbon, % Calc'd from Roller Cuts (a)	27.5	22.3	20.5	20.1	32.3	24.1
Roller, 0—20 Microns (b)	25 (25.1)	3 (17.8)	1 (16.9)	9 (28.7)	7 (32.2)	5 (28.8)
20—40 ,,	25 (28.1)	10 (26.2)	5 (21.3)	14 (23.6)	33 (32.5)	8 (21.4)
40—80 ,,	33 (28.9)	32 (24.6)	14 (20.5)	18 (21.3)	51 (32.2)	45 (24.6)
80+ ,,	17 (28.7)	55 (20.6)	80 (20.5)	59 (17.6)	9 (31.8)	42 (23.6)
Catalyst Balance, Wt. % (c)	101	100	96	101	98	100
Carbon Accumulation Rate (c)	540	430	394	93	690	158
Disintegration Rate (c) (e)	425	46	15	23	88	23
Disintegration Rate Index, %/Hr. (f)	6.8	3.1	0.36	0.13	5.6	0.37

(a) As received.
(b) Per cent carbon on roller cuts given in parentheses.
(c) C— and O— free.
(d) Grams carbon /100 g. catalyst/100 hours.
(e) Grams 0—20 microns/100 g. 20+ microns/hours.
(f) Correlates disintegration rate with the change in average particle size. Found to be most reliable expression of disintegration tendency.

It will observed that the disintegration index of catalysts pretreated with hydrogen at 900°—1200°F. is only a small portion of that of catalysts reduced at 700°F.

Heretofore the source of iron has been disclosed as mill scale, pyrites ash or synthetic ammonia catalyst. It is to be understood, however, that this invention and the method of forming catalyst may be applied to many other forms of iron, such as red iron oxide and various oxidic ores such as hematite, and sintered iron oxide particles as described and claimed in specification No. 620,775.

What we claim is:—

1. A process for the syntheses of hydrocarbons and oxygenated hydrocarbons by contacting a gas mixture containing hydrogen and carbon monoxide in a proportion of less than two molecules of hydrogen per molecule of carbon monoxide with a fluidized mass of finely divided iron catalyst particles at an elevated syntheses temperature and pressure, wherein the catalyst employed is prepared by subjecting fresh iron oxide to a reducing treatment with hydrogen at a temperature within the range of 900—1500°F. and subjecting the thus reduced catalyst, before use in the hydrocarbon syntheses reaction, to an activating or precarbiding treatment with a mixture containing hydrogen and carbon monoxide in a proportion of 2—8 molecules of hydrogen per molecule of carbon monoxide at a temperature between 500° and 700°F.

2. A process according to Claim 1,

wherein the treatment of the reduced catalyst with the hydrogen and carbon monoxide mixture is carried out until 50—55% by weight of the iron is converted into iron carbide.

3. A process according to Claim 1 or 2, wherein the reducing treatment with hydrogen is followed by a further reducing treatment with hydrogen at a temperature between 500° and 700°F. before the treatment with the mixture containing hydrogen and carbon monoxide.

4. A process according to any one of Claims 1—3, wherein the initial reduction of the catalyst is carried out so that the reduced catalyst contains from 3—10% by weight of oxygen based on iron.

5. A process according to any one of the preceding claims, wherein the iron oxide is pyrites ash or fused magnetite.

6. A process according to any one of the preceding claims, wherein the iron oxide is impregnated with a promotor.

7. A process according to Claim 6, wherein the promotor is sodium carbonate or a chloride, fluoride or carbonate of potassium.

Dated this 15th day of November, 1949.

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