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COMPLETE SPECIFICATION

Improved Process for the Catalytic Synthesis of Hydrocarbons

(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).

I, CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, 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:—

This invention relates to the catalytic conversion of carbon monoxides with hydrogen to form valuable synthetic products.

The conventional hydrocarbon synthesis processes may be divided into two broad classes, depending on the type of catalyst used and the character of reaction products obtained. One class comprises reactions using cobalt catalysts at relatively low temperatures of about 350°—450° F. and relatively low pressures of about 1—10 atm.abs. to form predominantly saturated paraffinic liquid and solid hydrocarbons from which highly valuable diesel fuels and lubricating oils but only low octane number motor fuels may be obtained. The other class of processes employs iron catalysts at higher temperatures of about 450°—800° F. and higher pressures of about 3—25 atm.abs. to obtain a predominantly unsaturated product from which highly valuable motor fuels having satisfactory octane ratings may be recovered. Also, in this class of processes pressures of up to 100 atmospheres or higher may sometimes be used, particularly if high yields of oxygenated compounds are desired. The present invention is concerned with that type of reaction which uses iron catalysts.

Active iron catalysts are usually prepared by the reduction of various iron ores or precipitated iron oxides as well as by the decomposition of iron carbonyls. The catalytic activity of the iron may be enhanced by the addition of such promoters as various compounds of alkali metals or the oxides of chromium, zinc, aluminium, magnesium, manganese, the rare earth metals, and others, in small amounts of about 1—10%. As an example of a proposed catalyst containing a promoting substance may be mentioned a catalyst comprising wholly or mainly a sintered metal of the iron group to which has been added an alkali compound which in aqueous solution has a neutral or acid reaction and which is practically undecomposed at temperatures up to 1000° C. As alkali compounds, alkali halides have been stated to be suitable and the addition to the above catalyst of potassium chloride, potassium bromide, sodium chloride or sodium fluoride has been specifically suggested.

It has further been proposed to carry out the catalytic hydrogenation and dehydrogenation of compounds containing carbon by employing catalytic agents containing metallic nickel, cobalt, iron or copper, and also fluorine, tellurium or antimony. Complex compounds of fluorine, tellurium or antimony have been reported to be advantageous for the above purpose, the use of potassium silico fluoride and potassium titanium fluoride having been specifically suggested. The present invention is directed solely to an improved process for the catalytic hydrogenation of carbon monoxide and it has now been found that the use in this process of a catalyst comprising a major proportion of an iron compound and a minor proportion of a fluorine compound gives exceptionally beneficial results as will become apparent hereinafter.

The essential factors determining the utility of an iron catalyst for hydrogenating carbon monoxide are total liquid yield as determined by activity (per cent.

conversion) and selectivity (ratio C_4 and higher hydrocarbons: C1 and higher hydrocarbons), olefin formation and catalyst stability. Thus, the average unpromoted iron catalysts have a selectivity of about 0.5, yielding about 140—150 cc. of liquid product per cu.m. of CO and H_2 consumed, which contains about 60—65% of olefin in the C_4 cut. These characteristics may be improved by the addition of the most active conventional promoters such as various potassium compounds, particularly potassium chloride and carbonate to a selectivity of somewhat less than 0.70, yielding about 200 cc. or less of liquid product per cu.m. of $CO + H_2$ consumed. The improvement of the olefin formation by the conventional alkali metal promoters is highly irregular. In view of the fact that the theoretical maximum yield of liquid hydrocarbons obtainable per cu.m. of synthesis gas containing 1 or 2 mols. of H_2 per mol. of CO is 290 cc. of liquid which may contain as much as 100% olefins in the C_4 cut, it will be appreciated that there is considerable room for improvement. However, in spite of the extensive research work conducted in the field of synthesis catalysts, no appreciable improvement is known to have been accomplished prior to the present invention beyond the figures given above. The present invention is chiefly concerned with such an improvement.

Accordingly the present invention consists of an improved process for producing normally liquid hydrocarbons from carbon monoxide and hydrogen by a catalytic synthesis reaction comprising contacting a gas mixture containing carbon monoxide and hydrogen in synthesis proportions, under synthesis conditions of temperature and pressure, with a catalyst comprising a major proportion of an iron component and a minor proportion of a fluorine compound of potassium as promoter.

While potassium fluoride is the preferred promoter other fluorine compounds of potassium particularly complex fluorides such as potassium aluminium fluoride and potassium fluosilicate may be used. The iron may be employed as an oxide, for instance in the form of red or yellow iron oxide, iron ores such as hematites, limonite and magnetite. The fluorine compound of potassium may be present in amounts of 0.1—10%, preferably about 1% of the iron oxide.

The catalysts may be prepared by moistening iron oxides with an aqueous potassium fluoride solution of suitable concentration followed by drying, sizing or otherwise forming. It may be advisable to add a small amount, such as 3—4% of a combustible binder, to aid in the pilling operation, and to remove the binder after pilling by roasting the catalyst in air at high temperatures of about 800°—1200° F. If desired, the impregnated iron oxide may be partially or substantially reduced by means of a reducing gas, such as hydrogen for about 2—6 hours at elevated temperatures of about 600°—1400° F. A sintering treatment in a non-oxidizing atmosphere at about 1000°—1800° F. for several hours may follow the reducing step. A typical method suitable for preparing the improved catalyst is as follows: 340 g. of a pigment form of red iron oxide (analyses—99.90% Fe_2O_3) is mixed with a solution of 3.4 g. potassium fluoride in 160 cc. of distilled water to form a paste. This paste is dried at 350° F., blended with 4% of a pilling aid (stearates) pilled and calcined 3 hours at 850° F. The pills are reduced for 3 hours with 1000 V/V/Hr. of hydrogen at 900° F. and then sintered in hydrogen for four hours at 1200° F.

While the procedure described above is a preferred method of preparing the catalysts it has been found that other methods may be used to incorporate fluorine compounds of potassium into the catalyst. For example, the catalysts may be prepared by treating iron or iron oxide containing a compound of potassium such as KOH, K_2CO_3 or KNO_3, with fluoriding materials such as H_2F_2 or FeF_3. Also the iron may be treated with these fluoriding materials first to introduce fluorine, and then be impregnated with KOH, K_2CO_3 or KNO_3. The catalyst base containing the potassium compound may be impregnated with aqueous solutions or treated with vapors of the volatile fluoriding agents at temperatures of about 100—500° C. Complex fluoriding materials such as fluosilicic acids or their salts may be used, as well as gaseous organic fluorides.

In carrying out the hydrocarbon synthesis in the presence of a catalyst of the type above described, conventional synthesis conditions for iron catalysts may be employed, for example temperatures of about 450°—850° F., preferably 500°—700° F., pressures of about 3—25 atm., H_2:CO ratios in the range of about 0.6:1 to 3:1 and space velocities of about 100—2500 V/V/hr.

The following data illustrate the advantages of the present improved process over procedures using iron catalysts promoted by the most active conventional potassium compounds such as potassium chloride, potassium carbonate and potassium sulphate. A series of comparative tests carried out on such miscellaneous catalysts prepared by methods similar to that described in the above specific example, at synthesis conditions of 250 lbs./sq. in. pressure, 200 V/V/hr. space velocity, 0.8—1.1 $H_2:CO$ feed ratio, and optimum reaction temperatures for the individual catalysts yielded the following results in fixed bed-operation.

TABLE I.

Catalyst (Reduced at 900° F. and Sintered at 1200° Before the tests	Temp. ° F.	Conv. % Output Basis	Selectivity C_4+/C_1+	Yields of C_4+, Output, cc./cu.m.	
				On Feed	On $CO+H_2$ Consumed
Red Fe_2O_3 + 1% KF	621	83	0.73	168	218
Red Fe_2O_3 + 1% KF (1)	530	98	0.71	171	205
Red Fe_2O_3 + 1% K_2CO_3	606	94	0.69	156	199
Red Fe_2O_3 + 1% KCL (2)	517	96	0.62	139	180
Red Fe_2O_3 + 1% KCL (3)	604	94	0.40	85	111
Red Fe_2O_3 + 1% K_3PO_4	600	98	0.61	158	177
Unpromoted Red Fe_2O_3	605	83	0.49	100	142

(1) Not sintered.
(2) Not sintered; operating pressure 150 psig.; this pressure change does not appreciably affect the yield.
(3) Sintered at 1300° F.

From the above data it will be appreciated that the process according to the present invention carried out in the presence of an iron catalyst promoted by potassium fluoride affords a considerable improvement with respect to selectivity and yield of liquid products which exceed those of the conventional procedures by as much as about 10—50%.

Tests carried out at optimum temperatures for olefin formation but at otherwise the same conditions as indicated in connection with Table I gave the following results:

TABLE II.

Catalyst (Reduced at 900° F. and Sintered at 1200° F.)	Synthesis Temp. ° F.	% Olefins in	
		C_4	C_5
99% Red Fe_2O_3, 1% KF	660	91	91
99% Red Fe_2O_3, 1% KF (1)	530	88	91
99% Red Fe_2O_3, 1% K_2CO_3	595	87	85
99% Red Fe_2O_3, 1% KCl (1)	500	68	69
99% Red Fe_2O_3, 1% KCl (2)	604	72	—
99% Red Fe_2O_3, 1% K_3PO_4	625	89	—
Red Iron Oxide Pigment (1) (3)	615	60	60

(1) Not sintered.
(2) Sintered at 1300° F.
(3) Reduced at 1000—1100° F.

It will be noted that the potassium fluoride-promoted catalyst yields the highest percentage of olefins and is the only one of the iron catalysts tested that affords a considerable increase of olefin formation in combination with maximum selectivity and maximum liquid yield.

With regard to olefin formation, it has been further found that the proportion of olefin produced by a KF-promoted iron catalyst increases with increasing reaction temperatures to reach a maximum at a temperature substantially higher, preferably about 10°—50° F. higher, than the optimum temperature for maximum liquid product yields. This phenomenon is the opposite of what should have been expected on the basis of the behaviour of unpromoted iron catalysts. Data pertinent hereto are given below, the lowest temperatures listed corresponding approximately to those of maximum liquid yield for the particular catalysts here involved.

TABLE III.

Catalyst	Temp. ° F.	Conv. %	Wt. % Olefins in C_4 Cut
Red Fe_2O_3, unpromoted	530	68	65
	550	92	58
	570	96	51
Red Fe_2O_3 + 1% KF	600	79	87
	630	88	89
	660	97	91

Therefore, if the formation of large proportions of olefins is desired, it is preferred to employ reaction temperatures above about 620° F. and preferably between about 630° and 680° F.

The present invention is not to be limited by any theory of the mechanism of the process or catalyst nor to the examples which are given merely for illustrative purposes.

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 producing normally liquid hydrocarbons from carbon monoxide and hydrogen by a catalytic synthesis reaction comprising contacting a gas mixture containing carbon monoxide and hydrogen in synthesis proportions, under synthesis conditions of temperature and pressure, with a catalyst comprising a major proportion of an iron component and a minor proportion of a fluorine compound of potassium.

2. A process as claimed in Claim 1, wherein the fluorine compound of potassium is potassium fluoride.

3. A process as claimed in Claim 1, wherein the fluorine compound of potassium is potassium fluoride complex such as potassium aluminum fluoride or potassium fluosilicate.

4. A process as claimed in any one of Claims 1—3, wherein the iron component is an iron oxide.

5. A process as claimed in Claim 4, wherein the iron oxide is red iron oxide, yellow iron oxide, or an iron ore, such as hematite, limonite, or magnetite.

6. A process as claimed in Claims 4 or 5, wherein the amount of the fluorine compound is from 0.1—10% by weight of the iron oxide.

7. A process as claimed in any one of Claims 1—6, wherein the catalyst composition is subjected to a reducing action with a reducing gas prior to use.

8. A process as claimed in Claim 7, wherein the catalyst composition is subjected to a sintering treatment in a non-oxidizing atmosphere, such as hydrogen, after the reducing action.

9. A process as claimed in any of the preceding claims, wherein the carbon monoxide-hydrogen mixture contains from 0.6—3 molecules of hydrogen per molecule of carbon monoxide and the reaction is carried out at a pressure of 3—25 atmospheres and at at a temperature considerably higher than the optimum temperature for producing maximum yields of liquid products.

10. A process as claimed in Claim 9, wherein the reaction temperature is 10—50° F. higher than the said optimum temperature.

11. A process as claimed in Claims 9 or 10, wherein the reaction is carried out at a temperature between 630 and 680° F.

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