

This invention is concerned with converting synthesis gas, i.e. mixtures of gaseous carbon oxides with hydrogen or hydrogen donors, to hydrocarbon mixtures.

Processes for the conversion of coal and other hydrocarbons, such as natural gas, to a gaseous mixture consisting essentially of hydrogen and carbon monoxide and/or dioxide are well known. Those of major importance depend either on the partial combustion of the fuel with an oxygen-containing gas or on the high temperature reaction of the fuel with steam, or on a combination of these two reactions. An excellent summary of the art of gas manufacture, including synthesis gas, from solid and liquid fuels is given in Encyclopedia of Chemical Technology, Edited by Kirk-Othmer, Second Edition, Volume 10, pages 353—433 (1966), Interscience Publishers, New York, New York.

It is also well known that synthesis gas will undergo conversion to reduction products of carbon monoxide, such as hydrocarbons, at from about 149°C (300°F) to about 454°C (850°F) under from about one to one thousand atmospheres pressure over a fairly wide variety of catalysts. The Fischer-Tropsch process, for example, which has been most extensively studied, produces a range of liquid hydrocarbons, a portion of which have been used as low octane gasoline. Catalysts that have been studied for this and related processes include those based on iron, cobalt, nickel, ruthenium, thorium, rhodium and osmium, or their oxides.

Recently, it has been discovered that the conversion of synthesis gas into valuable products can be greatly enhanced by employing a special type of crystalline aluminosilicate zeolite exemplified by ZSM-5 in admixture with a carbon monoxide reduction component. U.S. Patent 3,972,958 for example, describes a process in which synthesis gas is converted over a combination catalyst having as a first component a zeolite exemplified by ZSM-5 and as a second component a metal having good CO reducing activity and poor olefin-hydrogenation activity, such as Ru, Th, Rh, Fe or Co, at 149—427°C and 446—10443 kPa. That patent, however, is concerned primarily with the conversion of coal into gasoline and neither places special emphasis on nor specifically exemplifies the synthesis gas conversion step. A subsequent development is described in U.S. Patent 4,086,262 which involves the conversion of synthesis gas at elevated temperature over a catalyst which comprises an intimate mixture of a Fischer-Tropsch component and a special type of zeolite such as ZSM-5. That patent points out that the products are hydrocarbon mixtures which are useful in the manufacture of heating oil, high octane gasoline, aromatic compounds, and chemical intermediates.

Although U.S. Patent 4,086,262 is primarily

directed to multi-particle composite catalysts, i.e. the crystalline aluminosilicate component (one particle) is physically admixed with the Fischer-Tropsch component (another particle), nevertheless, Example 5 does disclose a single particle iron-containing catalyst (an alumina bound zeolite catalyst impregnated with iron). That catalyst consists of $\text{NH}_4\text{ZSM-5}$ and 35% alumina binder impregnated with ferric nitrate and calcined, and analyses to 3% iron. At 371°C, 3550 kPa and 30 seconds contact, synthesis gas of $\text{H}_2/\text{CO}=1$ produces 8.1 weight % hydrocarbons of which 33.4 weight % is CH_4 , 47.5 weight % is $\text{C}_2\text{—C}_4$ compounds and 19.1 weight % is C_5^+ compounds.

As can well be appreciated, the patent and technical literature relating to the Fischer-Tropsch process, is, indeed, extensive and the various catalysts reported in the prior art have been used by themselves as well as in admixture with catalytically inactive supports such as kieselguhr. Although the reasons for using catalytically inactive supports have varied, nevertheless, it would appear that one reason was that it resulted in increased surface area of the Fischer-Tropsch component deposited on it or admixed with it and that it also aided in controlling the heat requirements of the overall exothermic reactions.

It is also known in the art to admix a Fischer-Tropsch component with a material, such as silica-alumina which is known to be catalytically active for the conversion of hydrocarbons.

The present invention is based on the observation that synthesis gas can be converted in good yield and with good selectivity to a C_5^+ naphtha over an unpromoted, single particle iron-containing fluidized catalyst.

Accordingly, the present invention provides a process for converting synthesis gas into a naphtha product which comprises contacting synthesis gas at a temperature of 260 to 315°C, a pressure of 446 to 6996 kPa and a gas hourly space velocity of 400 to 20,000 with an unpromoted single particle fluidized catalyst comprising iron, a crystalline acidic aluminosilicate zeolite having a silica-to-alumina mole ratio of at least 12, a pore size greater than 5 Angstrom units and a constraint index of 1 to 12, and a siliceous matrix and prepared by adding the acidic zeolite to a siliceous hydrogel, homogenizing and spray drying the mixture to obtain fluid particles and impregnating the particles with a water-soluble iron salt, to obtain a hydrocarbon product containing not more than 30 weight % of methane plus ethane and at least 40 weight % of naphtha having a boiling range of less than 204°C at a 90% overhead being a C_5^+ naphtha having an aromatics content of 5 to 25 weight %.

The crystalline aluminosilicate zeolites which

form the basis of the fluid catalysts used in the process of the invention are fully described in U.S. Patent 4,086,262 referred to above. Preferred zeolites are ZSM-11 and ZSM-12 and, especially, ZSM-5.

The siliceous matrix portion of the single particle fluid catalyst is not narrowly critical and suitable matrices include silica, silica-zirconia and silica-magnesia. It has been found that one important criticality with regard to the matrix is that it should be siliceous. For reasons which are not completely understood, fluid catalysts that are formed with matrices based on alumina do not possess the physical characteristics required for fluidized processes. The total amount of alumina which is present in the finished catalyst in the process of this invention should preferably not exceed 30% by weight of the silica matrix in order to obtain a practical fluid process.

One surprising feature of the process of this invention is that the catalysts which are employed are unpromoted and yet they still exhibit high activity with little evident aging, and, in fact, are capable of converting syngas to the olefinic naphtha product previously described while producing no more than 30 weight percent of methane plus ethane, based on total hydrocarbons. In fact, the use of promoters, which the prior art found necessary in previous iron-containing catalysts, is definitely not preferred due to the fact that most promoters are alkaline in nature and they have a tendency to migrate to the acidic crystalline aluminosilicate zeolite component and to decrease the activity of the same. Therefore, it would appear that the single particle fluid catalyst used in the present invention represents a significant departure from the teachings of the prior art in that not only are promoters not necessary for sustained operation but, in fact are detrimental to the activity of the zeolitic component.

The single particle iron-containing fluid catalysts which are used in the process of this invention are prepared by adding the appropriate acidic crystalline aluminosilicate previously defined to a siliceous hydrogel before drying, homogenizing the same, thereafter spray-drying in order to obtain particles in the fluidized particle region, and impregnating with a water soluble iron salt such as iron nitrate.

It is to be understood that methods of making fluidized catalysts containing crystalline aluminosilicate zeolites and siliceous matrices are well known in the art and that no novelty is claimed in this step per se. Thus, for example, a composite of the crystalline aluminosilicate zeolite and a siliceous matrix can be made by admixing an aqueous alkali metal silicate with or without a particulate weighting agent, such as kaolin clay, desirably as a dispersion in water so as to intimately mix the clay particles with the alkali metal silicate. This admixing is conveniently done at room temperature, although,

of course, higher or lower temperatures may be employed if desired. The mixture is then heated, generally to a temperature of from 38—71°C (100—160°F) and acid is added to adjust the pH to from about 8—10. The temperature is maintained for a time of about 1—6 hours or longer. At this point, if a silica/zirconia weighting agent (e.g. clay) matrix is desired, a zirconium salt is added, desirably as an aqueous solution thereof. Acid is then added to reduce the pH to about 4—7 and form a silica gel/weighting agent or a silica gel-zirconia gel/weighting agent slurry, which is then admixed with a slurry of the acidic crystalline aluminosilicate zeolite previously described. The resulting composite is then homogenized and spray dried to produce fluid size particles which are then treated with a source of ammonium ions or hydrogen ions in order to reduce the sodium content to a low level which is desirably less than about 0.1% sodium.

The fluid particles are thereafter impregnated with an aqueous solution of a water-soluble iron salt, which is preferably iron nitrate in order to form the finished single particle catalyst of this invention. As is generally known in fluid catalysts for catalytic cracking, the catalyst preferably additionally includes a weighting agent. The most preferred weighting agent is kaolin clay. Other weighting agents may be substituted in whole or in part for the kaolin clay so long as the weighting agents are not detrimental to the finished catalyst. It is to be understood, however, that the amount of clay which is added as a weighting agent should not be so great that the total catalyst composite contains more than 30% by weight of alumina.

The relative proportion of crystalline aluminosilicate zeolite to matrix is not narrowly critical and it can range from about 5—40 weight percent of the matrix.

As has been indicated earlier, the crystalline aluminosilicate zeolite and a matrix are then thoroughly mixed in a form of an aqueous slurry in order to homogenize the same and thereafter subdivided and dried to form the desired particles. A particularly good method of making microspherical particles (e.g. of particle size of about 1—200 microns) especially suitable for use in the fluidized process of this invention is spray-drying.

The temperature of air (or other gas) entering the spray drier is ordinarily within the range of 260 to 538°C (500—1,000°F). The temperature used will depend on such factors as the quantity of material to be dried and the quality of air used in the drying. The evaporation rate will vary depending on the quantity of air used in the drying. The temperature of the particles which are being dried is generally within the range of 65—204°C (150—400°F) at the completion of the drying, but preferably 93—177°C (200—350°F).

The drying may be affected by a process in which the particles to be dried and a hot air

stream are moving in the same direction for the entire drying period (concurrent drying) or where the hot stream flows in the opposite direction (countercurrent drying), or by semi-concurrent drying. It is to be understood that spray-drying to form fluidized catalysts is well known in the art and a representative procedure is described in United States 3,553,104, the entire contents of which are incorporated by reference.

In order to complete the preparation of the single particle fluid catalyst of this invention, the spray-dried material above-described is thereafter impregnated with an aqueous solution of an iron salt. The particular iron salt employed is not narrowly critical and can include the nitrate, the chloride, the sulfate or the acetate. It is to be understood, however, that the nitrate is preferred due to the fact that other salts such as the sulfate are sometimes harmful to the overall catalyst unless great care is taken to remove all the residual sulfate ion by washing.

The amount of iron oxide which is contained in the finished catalyst can range from 2.5—25 weight percent, based on the weight of the total catalyst, with 10—20% being preferred.

The iron impregnated catalyst is thereafter usually calcined in air at elevated temperatures for periods of time ranging from 1—24 hours in order to convert the iron to iron oxide followed by treatment with hydrogen or syngas.

The acidic crystalline aluminosilicate component of the catalyst is characterized by a pore dimension greater than about 5 Angstroms, i.e. it is capable of sorbing paraffins, and it has a silica-to-alumina ratio of at least 12 and a constraint index within the range of 1 to 12. Zeolite A, for example, with a silica-to-alumina ratio of 2.0 is not useful in this invention, and it has no pore dimension greater than about 5 Angstroms.

The crystalline aluminosilicates herein referred to, also known as zeolites, constitute an unusual class of natural and synthetic minerals. They are characterized by having a rigid crystalline framework structure composed of an assembly of silicon and aluminum atoms, each surrounded by a tetrahedron of shared oxygen atoms, and a precisely defined pore structure. Exchangeable cations are present in the pores.

The acidic crystalline aluminosilicate component preferably is in the hydrogen form.

The catalysts referred to herein utilize members of a special class of zeolites exhibiting some unusual properties. They are very active even with silica-to-alumina ratios exceeding 30. This activity is surprising since catalytic activity of zeolites is generally attributed to framework aluminum atoms and cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam even at high temperatures which induce irreversible collapse of the crystal framework of other zeolites, e.g. of the X and A type. Furthermore,

carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity. In many environments the zeolites of this class exhibit very low coke forming capability, conducive to very long times on stream between burning regenerations.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from, the intra-crystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred zeolites useful in this invention comprise, in combination: a silica-to-alumina ratio of at least about 12; and a structure providing constrained access to the crystalline free space.

The silica-to-alumina ratio referred to may be determined by conventional analysis. This ratio is meant to represent as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica-to-alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The zeolites useful as catalysts in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, their structure must provide constrained access to some larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access by molecules of larger cross-section than normal hexane is substantially excluded and the zeolite is not of the desired type. Zeolites with windows of 10-membered rings are preferred, although excessive puckering or pore blockage may render these zeolites substantially ineffective. Zeolites with windows of 12-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions desired in the instant invention, although structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal

structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by continuously passing a mixture of equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 538°C (1,000°F) for at least 15 minutes. The zeolite is then flushed with helium and the tem-

perature adjusted between 288°C (550°F) and 510°C (950°F) to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of catalyst per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10} (\text{fraction of n-hexane remaining})}{\log_{10} (\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Catalysts suitable for the present invention are those which employ a zeolite having a constraint index from 1.0 to 12.0. Constraint Index (CI) values for some typical zeolites including some not within the scope of this invention are:

CAS	C.I.
Erionite	38
ZSM-5	8.3
ZSM-11	8.7
ZSM-35	6.0
TMA Offretite	3.7
ZSM-38	2.0
ZSM-12	2
Beta	0.6
ZSM-4	0.5
Acid Mordenite	0.5
REY	0.4
Amorphous silica-alumina	0.6

The above-described Constraint Index is an important and even critical, definition of those zeolites which are useful to catalyze the instant process. The very nature of this parameter and the recited technique by which it is determined, however, admit of the possibility that a given zeolite can be tested under somewhat different conditions and thereby have different constraint indexes. Constraint index seems to vary somewhat with severity of operation (conversion). Therefore, it will be appreciated that it may be possible to so select test conditions to establish multiple constraint indexes for a particular given zeolite which may be both inside and outside the above-defined range of 1 to 12.

Thus, it should be understood that the parameter and property "Constraint Index" as such value is used herein as an inclusive rather than an exclusive value. That is, a zeolite when tested by any combination of conditions within the testing definition set forth hereinabove to have a constraint index of 1 to 12 is intended to

be included in the instant catalyst definition regardless that the same identical zeolite tested under other defined conditions may give a constraint index value outside of 1 to 12.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38, respectively defined by the x-ray diffraction data presented in U.S. Specifications 3,702,886, 3,709,979, 3,832,449, 4,016,245 and 4,046,859.

The process of this invention is carried out at temperatures ranging from about 260°C (500°F) to 315°C (600°F) and more preferably from 288°C (550°F) to 304°C (580°F). The process of this invention is carried out at gas hourly space velocities (GHSV), ranging from 400—20,000 and more desirably from 500 to 6,000, based on fresh feed and total catalyst volume. Hydrogen to carbon oxides ratios can vary from 0.5:1 to 2:1 and more preferably are about 1:1. Pressures ranging from 446 kPa (50 psig) to 6996 kPa (1000 psig) and more preferably 1135 kPa (150 psig) to 2859 kPa (400 psig) are employed.

The following examples will illustrate the process of this invention.

Example 1

A silica-clay hydrogel was prepared by adding 153.2 cc of 97.1% sulfuric acid to a slurry of 698 grams of WP kaolin clay in 32.4 lbs of demineralized water and 2989 grams of Q-Brand sodium silicate (containing 8.9% wt. Na₂O and 28.7% wt. SiO₂) at 48—88°C (120°F). After heating the mixture to 60°C (140°F) for two hours a solution containing 52.3 grams of aluminum sulfate in 209 cc of water was added, followed by 66.8 grams of sodium zirconium silicate in 648 cc water and the pH adjusted to 4.7 by adding sulfuric acid. After standing overnight the equivalent of 40% HZSM-5 was added and the resulting gel was homogenized and spray dried, NH₄⁺ exchanged and washed until <.01% Na. The composition of the hydrogel on a solids basis was approxi-

mately 54.5% SiO₂, 0.5% Al₂O₃, 1% ZrO₂, and 44% clay.

Example 2

Ten grams of the matrix prepared in Example 1 was impregnated with 12.5 grams of Fe(NO₃)₃ · 9H₂O dissolved in 6.0 cc H₂O. The catalyst after drying at 121°C (250°F) and calcining in air at 1000°F for three hours contained 13.4% iron. One portion of this catalyst (Ex. 2a) was conditioned in hydrogen while Ex. 2b was conditioned in CO+H₂.

Example 3

Q-Brand sodium silicate solution (7972.9 grams) was added to a slurry of 1866.4 grams Georgia kaolin (WP) clay in 86.4 lbs of water. The mixture was heated to 49°C (120°F) and 408.4 cc of 97.1% sulfuric acid was added, followed by heating to 60°C (140°F) for two hours. After cooling, 139.5 grams of aluminum sulfate in 558.1 cc H₂O was mixed in, followed by 178.0 g sodium zirconium silicate in 1730 cc H₂O. After adjusting to pH 4 with H₂SO₄, 1333 grams of HZSM-5 zeolite was added to one-half of the gel mass.

Example 4

The catalyst in this example was prepared by impregnating 10 grams of the fluid matrix prepared in Example 1 with a solution of 9.2 grams ferric nitrate 9-hydrate in 6 cc of water. After drying at 121°C (250°F) and calcining at 538°C (1000°F) the catalyst analyzed for 11.3% iron.

Example 5

In a similar manner this catalyst was prepared by impregnating 10 grams of the fluid matrix of Example 3, with 4.6 grams Fe(NO₃)₃ · 9H₂O dissolved in 6 cc of water. After drying and calcination in air at 538°C (1000°F) the finished catalyst contained 5.5% iron.

Example 6

This catalyst was prepared in a similar manner using the fluid matrix of Example 1 and contained 15.7% iron in the finished form.

Example 7

The fluid catalyst matrix of this example was

prepared in the following manner. Q-Brand silicate solution (7972.2 grams) was added to a water slurry containing 1861 grams WP kaolin clay in 83.7 lbs of water. After heating 49°C (120°F) 752.4 grams of 97% H₂SO₄ was added and the resulting hydrogel heated to 60°C (140°F) for two hours. A solution containing 139.4 grams aluminum sulfate in 560 cc water was added, followed by 166.7 grams sodium zirconium silicate solution. The mixture was acidified with H₂SO₄ to a pH of 4.7 and left to stand overnight. After removal of 2000 grams of the gel for other studies, 2563 grams of the ammonium form of ZSM-5 slurried with 8000 cc H₂O was added to the remainder of the gel, and the mixture homogenized and spray dried. The gel was exchanged twice with 6 lbs of ammonium sulfate in 40 lbs H₂O and washed until free of sulfate, followed by drying at 121°C (250°F). The Na content was less than 0.01%.

Example 8

This catalyst was prepared by impregnating the fluid matrix of Example 7 with a solution containing 1875 gm Fe(NO₃)₃ · 9H₂O in 900 cc of water. After tumble drying at 121°C (250°F) a final air calcination for 3 hours at 538°C (1000°F) gave the finished catalyst, which contained 13.0% iron. Other properties are listed in the following table:

TABLE
Properties of iron-ZSM-5 fluid syn gas catalyst
of Example 8

Composition, Wt. %	
SiO ₂	66.8
Al ₂ O ₃	9.5
Fe ₂ O ₃	18.6
ZrO ₂	1.5
HZSM-5	35
SiO ₂ /Al ₂ O ₃ (zeolite)	70/1
Surface area	240 m ² /g
Particle density	1.6 g/cc
Real density	2.7 g/cc
Packed density	0.48 g/cc
Pore volume	0.54 cc/g

The catalysts were evaluated for the conversion of syngas to gasoline at 1480 kPa (200 psig) and 1:1 CO/H₂ ratio.

Example	2a	2b	4 day 2
Run time, hours	43	20	21
GHSV	807	754	1128
WHSV	1.00	1.01	1.32
Temp. °C average	290 (555°F)	293 (560°F)	323 (615°F)
Hot spot	301 (574°F)	299 (571°F)	335 (635°F)
CO Conversion, wt. %	30.7	48.3	47.0
H ₂ Conversion, wt. %	45.2	53.3	44.3
% Wt. C converted to: Hydrocarbon	75.8	66.7	72.5

Example	2a	2b	4 day 2
Product yield, wt. %			
HC	10.9	15.2	13.6
H ₂ O	9.9	10.0	5.7
H ₂	3.9	3.3	4.1
CO	64.4	48.1	49.1
CO ₂	10.8	23.4	27.5
Hydrocarbon composition, wt. %			
C ₁	19.6	15.1	31.7
C ₂	7.1	6.7	10.2
C ₃	5.1	3.6	4.0
C ₄	12.2	10.0	11.7
C ₅	11.5	11.4	7.2
C ₆	44.5	53.2	35.2
Olefins, wt. % by C No.			
C ₂ =	37.4	42.4	17.4
C ₃ =	44.2	40.4	9.7
C ₄ =	58.4	50.8	30.7
C ₅ =	71.2	61.1	37.5
C ₅ Olefin distribution, wt. %			
C ₅ =1	1.9	2.1	1.6
2M1C ₄ =	17.4	17.5	15.5
3M1C ₄ =	1.3	1.5	1.1
T2C ₅ =	11.5	12.1	11.7
C ₂ C ₅ =	5.8	6.1	5.7
2M2C ₄ =	62.1	60.7	50.4
C ₆ + Aromatics, wt. %	4.5	8.2	10.7
Liq. prod. 90% Pt. °C (D-2887)	180 (356°F)	181 (358°F)	182 (360°F)
Conditioned in H ₂ , °C/hr.	504 (940°F)/16		510 (950°F)/16
Conditioned in 1:1 COH ₂ , °C/hr.		318 (605°F)/65	

Example	4 day 8	5 day 2	5 day 4
Run time, hours	21	18.5	19
GHSV	884	971	951
WHSV	1.00	1.33	1.35
Temp. °C average	299 (571°F)	318 (604°F)	320 (609°F)
Hot spot	306 (583°F)	324 (615°F)	325 (617°F)
CO Conversion, wt. %	43.4	20.8	19.5
H ₂ Conversion, wt. %	44.9	35.1	28.6
% Wt. C converted to:	80.9	76.0	74.9
Hydrocarbon			
Product yield, wt. %			
HC	15.2	8.1	7.9
H ₂ O	9.2	6.6	5.2
H ₂	3.9	5.1	5.2
CO	52.6	73.0	74.6
CO ₂	19.1	7.3	7.1
Hydrocarbon composition, wt. %			
C ₁	22.0	24.2	26.5
C ₂	8.1	9.5	10.1
C ₃	3.7	4.7	5.5
C ₄	8.4	13.3	13.4
C ₅	8.4	8.5	9.7
C ₆ +	49.3	39.7	34.8

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Example	4 day 8	5 day 2	5 day 4
Olefins, wt. % by C No.			
C ₂ =	23.7	31.8	30.1
C ₃ =	17.5	16.0	27.6
C ₄ =	45.8	33.8	42.2
C ₅ =	61.4	35.7	43.6
C ₅ Olefin distribution, wt. %			
C ₅ =1	1.4	0	1.5
2M1C ₄ =	15.2	16	14.2
3M1C ₄ =	1.0	0	0.9
T2C ₅ =	11.2	12	11.5
C ₂ C ₅ =	5.3	4	5.4
2M2C ₄ =	65.9	68	66.5
C ₈ + Aromatics, wt. %	8.3	11.4	8.5
Liq. prod. 90% Pt °C (D-2887)	188 (370°F)	180 (357°F)	168 (335°F)
Conditioned in H ₂ , °C/hr.		510 (950°F)/16	
Conditioned in 1:1 CO/H ₂ , °C/hr.			

Example	6	8
Run time, hours	20	42
GHSV	924	986
WHSV	1.01	1.06
Temp., °C, average	290 (555°F)	290 (555°F)
Hot spot	302 (575°F)	303 (577°F)
CO Conversion, wt.	52.4	68.2
H ₂ Conversion, wt. %	54.9	61.4
% wt. C converted to:	64.7	59.1
Hydrocarbon		
Product yield, wt. %		
HC	15.5	19.0
H ₂ O	10.0	8.0
H ₂	3.2	2.7
CO	44.3	29.6
CO ₂	27.0	40.7
Hydrocarbon composition, wt. %		
C ₁	15.4	16.9
C ₂	7.0	7.2
C ₃	4.0	3.8
C ₄	9.2	9.7
C ₅	10.7	9.9
C ₆ +	53.6	47.6
Olefins, wt. % by C No.		
C ₂ =	41.6	19.9
C ₃ =	41.5	11.0
C ₄ =	55.4	33.3
C ₅ =	66.4	41.5
C ₅ Olefin distribution, wt. %		
C ₅ =1	2.0	2.0
2M1C ₄ =	17.1	17.3
3M1C ₄ =	1.4	1.4
T2C ₅ =	12.0	12.0
C ₂ C ₅ =	6.1	5.9
2M2C ₄ =	61.5	61.3
C ₈ + Aromatics, wt. %	6.8	10.3
Liq. prod. 90% Pt., °C (D-2887)	182 (359°F)	184 (364°F)
Conditioned in H ₂ , °C/hr.		
Conditioned in 1:1 CO/H ₂ , °C/hr.	315 (600°F)/70	315 (600°F)/66

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Claims

1. A process for converting synthesis gas into a naphtha product which comprises contacting synthesis gas at a temperature of 260 to 315°C, a pressure of 446 to 6996 kPa and a gas hourly space velocity of 400 to 20,000 with an unpromoted single particle fluidized catalyst comprising iron, a crystalline acidic aluminosilicate zeolite having a silica-to-alumina mole ratio of at least 12, a pore size greater than 5 Angstrom units and a constraint index of 1 to 12, and a siliceous matrix and prepared by adding the acidic zeolite to a siliceous hydrogel, homogenizing and spray drying the mixture to obtain fluid particles and impregnating the particles with a water-soluble iron salt, to obtain a hydrocarbon product containing not more than 30 weight % of methane plus ethane and at least 40 weight % of naphtha having a boiling range of less than 204°C at a 90% overhead being a C₅⁺ naphtha having an aromatics content of 5 to 25 weight %.

2. A process according to claim 1 wherein said catalyst further contains a clay weighting agent.

3. A process according to claim 1 or 2 wherein the acidic zeolite is ZSM-5.

4. A process according to any preceding claim wherein the iron salt is iron nitrate.

5. A process according to any preceding claim wherein the weight of the zeolite which the catalyst contains is 5 to 40 percent of the weight of the matrix.

Revendications

1. Procédé pour la conversion de gaz de synthèse en un naphta, qui consiste à mettre en contact le gaz de synthèse à une température de 260 à 315°C, sous une pression de 446 à 6996 kPa et à une vitesse spatiale horaire du gaz de 400 à 20 000, avec un catalyseur fluidisé monoparticulaire non activé comprenant du fer, une zéolite du type aluminosilicate acide cristallin ayant un rapport molaire silice/alumine d'au moins 12, une dimension de pores de plus de 5 Å et un indice de contrainte de 1 à 12, et une matrice siliceuse et préparé par addition de la zéolite acide à un hydrogel siliceux, homogénéisation et séchage par pulvérisation du mélange pour obtenir des particules fluides et imprégnation des particules avec un sel de fer soluble dans l'eau, pour obtenir un hydrocarbure contenant pas plus de 30% en poids de méthane+éthane et au moins 40% en poids de naphta ayant un intervalle d'ébullition inférieur à 204°C avec avec 90% de têtes con-

sistant en naphta en C₅⁺ ayant une teneur en aromatiques de 5 à 25% en poids.

2. Procédé selon la revendication 1, caractérisé en ce que ledit catalyseur contient en outre un agent de lestage du type argile.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que la zéolite acide est la ZSM-5.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le sel de fer est le nitrate de fer.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le poids de zéolite contenu dans le catalyseur est de 5 et 40% du poids de la matrice.

Patentansprüche

1. Verfahren zur Umwandlung von Synthesegas in ein Naphthaprodukt, dadurch gekennzeichnet, daß man Synthesegas bei einer Temperatur von 260 bis 315°C, einem Druck von 466 bis 6996 kPa und einer stündlichen Gasraumströmungsgeschwindigkeit von 400 bis 20 000 mit einem unaktivierten bzw. undotierten fluidisierten Einzelpartikel-Katalysator, enthaltend Eisen, einen kristallinen sauren Aluminosilicat-Zeolithen mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von wenigstens 12, einer Porengröße von mehr als 5 Angström-Einheiten und einem Zwangsindex von 1 bis 12 und ein siliciumhaltiges Grundmaterial und hergestellt durch Zugabe des sauren Zeolithen zu einem siliciumhaltigen Hydrogel, Homogenisieren und Sprühtrocknen des Gemisches zur Erzielung von Fluidpartikeln und Imprägnieren der Partikel mit einem wasserlöslichen Eisensalz, zur Erzielung eines Kohlenwasserstoffproduktes in Berührung bringt, enthaltend nicht mehr als 30 Gew.-% Methan plus Äthan und wenigstens 40 Gew.-% Naphtha mit einem Siedebereich von weniger als 204°C bei einem 90%-Überkopfprodukt aus einem C₅⁺-Naphthaprodukt mit einem Aromatengehalt von 5 bis 25 Gew.-%.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Katalysator weiterhin ein Tonerde-Beschwerungsmittel enthält.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der saure Zeolith ZSM-5 ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Eisensalz Eisennitrat ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Gewicht des Zeolithen, der den Katalysator enthält, 5 bis 40 Gew.-% des Grundmaterials beträgt.

