

①②

EUROPEAN PATENT APPLICATION

②① Application number: 81301167.3

⑤① Int. Cl.³: **C 07 C 1/04**
B 01 J 29/30

②② Date of filing: 18.03.81

③① Priority: 24.03.80 US 133384

④③ Date of publication of application:
07.10.81 Bulletin 81/40

⑥④ Designated Contracting States:
BE DE FR GB IT NL

⑦① Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017(US)

⑦② Inventor: **Land, William Harry**
Box 245 A RD 1 Mount Rose Road
Pennington New Jersey 08534(US)

⑦② Inventor: **Chang, Clarence Dayton**
11 Murray Place
Princeton New Jersey 08540(US)

⑦④ Representative: **Cooper, John Anthony et al,**
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

⑤④ **Conversion of synthesis gas into hydrocarbons rich in linear alpha-olefins.**

⑤⑦ Hydrocarbons rich in linear alpha-olefins are produced by contacting synthesis gas at elevated temperatures with a ZSM-5 type zeolite which is substantially catalytically inert and which contains within its pores a carbon oxide-reducing component, for example a Fischer-Tropsch type catalyst such as iron, cobalt or ruthenium.

EP 0 037 213 A1

CONVERSION OF SYNTHESIS GAS
INTO HYDROCARBONS RICH IN LINEAR ALPHA-OLEFINS

This invention relates to an improved process for converting synthesis gas, i.e. mixtures of gaseous carbon oxides and hydrogen or hydrogen donors (also known as syngas), into hydrocarbon mixtures rich in linear alpha-olefins utilizing a catalytically inactive (i.e. substantially non-acidic) zeolite of the ZSM-5 type onto which is deposited a carbon oxide-reducing component.

Processes for the conversion of coal and other hydrocarbons, such as natural gas, into a gaseous mixture consisting essentially of hydrogen and carbon monoxide and/or carbon 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 into reduction products of carbon monoxide, such as hydrocarbons, at from about 148°C to about 455°C, 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, and their oxides.

Recently, it has been discovered that the conversion of synthesis gas into valuable products can be greatly enhanced by employing crystalline zeolites exemplified by ZSM-5 in admixture with a carbon monoxide reduction catalyst. Thus, for example, in United States Patent 4,086,262, there is disclosed a process for the conversion of syngas by passing syngas at elevated temperature over a catalyst which comprises an intimate mixture of a Fischer-Tropsch component and a zeolite such as ZSM-5. That patent points out that the products produced are hydrocarbon mixtures which are useful in the manufacture of heating oil, high octane gasoline, aromatic compounds, and chemical intermediates.

Although United States Patent 4,086,262 is directed primarily to multi-particle composite catalysts, i.e. the crystalline zeolite component (one particle) is physically admixed with the Fischer-Tropsch component (another particle), nevertheless, Example 5 of that patent does disclose an iron-impregnated, ammonium-exchanged ZSM-5 in an alumina matrix.

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 for using them was that they result in increased surface area of the Fischer-Tropsch component which has been deposited on or admixed with them and that they also aid in controlling the heat-requirements of the overall exothermic reactions.

The process of this invention is directed towards an improvement in the process of converting syngas into a very specific product, namely, one that is rich in linear alpha-olefins. As stated above, the concept of contacting

syngas with ZSM-5 type zeolites containing carbon oxide-reducing components is known in the art. In this connection, United States Patent 4,086,262, referred to above as well as United States Patent 4,096,163, disclose processes for conversion of syngas utilizing ZSM-5 type zeolites in admixture with carbon oxide-reducing components, such as Fischer-Tropsch materials.

However, all the above-mentioned prior art involves the use of ZSM-5 type zeolites which were catalytically active i.e. were acidic. As is well known in the art, an acidic material has the ability to catalyze the transformation of hydrocarbons into different products.

The present invention is concerned with a substantially catalytically inactive support and is directed towards the concept of using the particular pore diameters of a ZSM-5 type zeolite in order to direct the conversion of syngas into a particular product, namely, one which is rich in linear alpha-olefins. Thus, this invention is not concerned with conventional acid catalysis, but rather with the use of substantially catalytically inactive materials which influence the selectivity or course of reactions when used as a catalyst support for carbon oxide-reducing materials such as Fischer-Tropsch components.

Accordingly, the present invention provides a process for the conversion of synthesis gas into hydrocarbons by contacting synthesis gas at an elevated temperature with a ZSM-5 type zeolite and a carbon oxide-reducing component, wherein the ZSM-5 type zeolite is substantially catalytically inert and contains the carbon oxide-reducing component within the pores thereof.

The process of this invention enhances the selectivity of the product to linear alpha-olefins, in general, and more especially to C₄-C₆ olefins. Linear alpha-olefins are very valuable products and can be used

in a wide variety of chemical processes as is well known in the art, such as the production of soaps and lubricating oils, for example.

Another significant difference between the process of this invention and the previously practiced processes for the conversion of syngas involving ZSM-5 type zeolites resides in the fact that the specific products will not be obtained merely by using physical mixtures of ZSM-5 and carbon oxide-reducing components. In the vast majority of Fischer-Tropsch conversion processes involving ZSM-5 type zeolites, mixtures of discrete particles are utilized in order to effect the transformation of a syngas into various products, either rich in olefins or rich in aromatics. As will be illustrated below by specific examples, in order to obtain the required distribution of linear alpha-olefins in the process of this invention, it is necessary that the carbon oxide-reducing component, i.e. iron, cobalt or ruthenium, be present within the pores of the ZSM-5 type zeolite. In this connection, methods for including carbon oxide-reducing components within the pores of ZSM-5 type zeolites are known in the art and the preferred technique involves impregnation of the zeolite with an aqueous solution of a salt of the desired metal. The nature of the salt is not critical and any water-soluble salt such as the chloride, sulfate, or nitrate can be utilized although in the examples which follow, the nitrate was the salt employed.

The expression "ZSM-5 type zeolites" used throughout this specification is intended to include the zeolites ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38, as well as all materials having the x-ray diffraction patterns of these zeolites irrespective of chemical composition.

ZSM-5 is more fully described in United States Patent 3,702,886; ZSM-11 is more particularly described in United States Patent 3,702,979; ZSM-12 is more

F-0481-L

-5-

particularly described in United States Patent 3,832,449; ZSM-35 is described in United States Patent 4,016,245; and ZSM-38 is described in United States Patent 4,046,859.

As stated above, it is essential to the process of this invention that the ZSM-5 type zeolite be substantially catalytically inert so that it will perform a sieving function only, as opposed to a catalytic transformation of the hydrocarbons produced from syngas conversion. Stated in another way, the ZSM-5 type zeolite should be substantially non-acidic. In order to obtain this condition, various techniques can be utilized. It is known in the art that the greater the aluminum content in the skeletal structure of a ZSM-5 type zeolite, the greater opportunity there is to have exchangeable sites which can be acidic. Conversely, the lower the aluminum content, the less availability there is to provide acid sites via base exchange or other techniques. Therefore, if the ZSM-5 type zeolite which is used is substantially free of alumina, i.e. if it has a silica-to-alumina ratio of greater than about 1600, then no particular caution ordinarily need be taken and such material can be utilized in the "as synthesized state" for the reason that the material simply does not have sufficient inherent acidity to be catalytically active under the reaction conditions of this invention. On the other hand, if ZSM-5 type zeolites of fairly high alumina content are utilized, i.e. if they have silica-to-alumina ratios less than 1600, special precautions must be taken to ensure that the zeolite is substantially catalytically inert. In order to achieve this, the zeolite can be base exchanged with alkali metal cations, preferably sodium, in order substantially to eliminate all acidity.

In this connection, a special test has been devised to measure the acidity of various candidate catalysts in order to determine whether or not they are

operable in the process of this invention. The test involves measuring the rate of cyclopropane isomerization and comparing it against 46 A.I. silica-alumina as a reference standard.

The test procedure involves utilizing a 5 to 250 mg. sample of the zeolite having a particle size of 20 to -200 mesh and mixing it with about 1 ml of Vycor chips and loading into a 5 mm inside diameter Vycor reactor tube which is heated in air at a flow rate of 150 ml per minute to 538°C and maintained there for 30 minutes. The sample is then cooled to 250°C in helium at a flow rate of 12-80 ml per minute. Cyclopropane (helium/cyclopropane, 4, vol. to vol.) is then introduced and the reactor effluent analyzed by gas chromatographic techniques. The contact time is adjusted to keep the conversion within the range 0.5 to 50%. Since it is well known in the literature that the isomerization of cyclopropane is first order, rate constants may be determined at several temperatures to check for diffusional limitations. Using the above technique, the first order rate constant for the standard 46 A.I. silica-alumina catalyst is 63.3 second^{-1} at 250°C. This value was arbitrarily assigned an index of 1,000 so as to serve as a reference value. Thus, the cyclopropane isomerization index (C.P.I. Index) for a candidate catalyst with a first order rate constant of 0.633 would be determined as follows:

$$\frac{1,000 \times 0.633}{63.3} = 10$$

Thus, the expression "substantially catalytically inert" as used throughout this specification is intended to define a zeolite which has a C.P.I. Index of no greater than 10 as measured by the above test.

The following table lists the values obtained when subjecting various materials, including crystalline zeolites, to the cyclopropane isomerization test described above.

TABLE 1Cyclopropane Isomerization (CPI) Index

<u>Materials</u>	<u>k, sec⁻¹ 250°C</u>	<u>CPI</u>
1. MgPHZSM-5	151	2400
2. 46 A.I. Si/Al, Ref. Std.	63.3	1000
3. ZrO ₂	60.2	950
4. HZSM-5, SiO ₂ /Al ₂ O ₃ = 1670	50.0	790
5. KHZSM-5	3.98	63
6. NaZSM-5, SiO ₂ /Al ₂ O ₃ = 70 (exchanged with NaHCO ₃)	1.36	21
7. NaHZSM-5, SiO ₂ /Al ₂ O ₃ = 1670	0.441	7.0
8. NaZSM-5, SiO ₂ /Al ₂ O ₃ = 600	0.125	2.0
9. NaZSM-5, SiO ₂ /Al ₂ O ₃ = 1670	0.050	0.8
10. FeNaZSM-5, SiO ₂ /Al ₂ O ₃ = 1600	0.021	0.3

From the Table, it can be seen that there are ZSM-5 zeolites which are operable in the process of this invention, i.e. which have a C.P.I. Index of no greater than 10, as well as ZSM-5 type materials which are inoperable in the process of this invention. Thus, for example, Material No. 1 is a magnesium/phosphorous-exchanged ZSM-5 and, as can be seen, its acidity is higher than that of the 46 A.I. reference standard. Material No. 4 is an acid-exchanged ZSM-5 zeolite having a silica-to-alumina ratio of 1670 and, as can be seen, this material is also inoperable in the process of this invention. Material No. 5 is a potassium-exchanged acid ZSM-5 and Catalyst No. 6 is a sodium exchanged ZSM-5, but they simply have not been exchanged with enough alkali metal to lower their acidity. Materials, 7, 8, 9 and 10 all possess a sufficiently low C.P.I. Index to be potential candidates for the process of this invention, providing of course

that a Fischer-Tropsch component is introduced within the pores thereof. In this connection, Material No. 10 is the very material which formed the basis for the catalyst tested in Example 1.

The process of this invention is carried out at temperatures ranging from about 260 to 343°C and more preferably from 287 to about 316°C. The process of this invention is carried out at gas hourly space velocities (GHSV) ranging from 400 to 20,000 and more desirably from 500 to 6,000, based on fresh feed and total catalyst volume. Hydrogen to carbon oxide ratios can vary from 0.5:1 to 2:1 and more preferably are about 1:1, the pressures ranging from 3.4 to 68 atmospheres gage and more preferably from 10.2 to 27.2 atmospheres gage.

The following Examples illustrate the invention.

EXAMPLES 1-8

In these Examples, various materials were evaluated for the conversion of synthesis gas as follows:

- Example 1 ZSM-5 having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 1600 and a sodium content of about 1.6 weight percent, impregnated with an aqueous solution of iron nitrate to 1.0 weight percent iron.
- Example 2 Same as Example 1, except that 1 weight percent of potassium is added.
- Example 3 Sodium mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 93 and a sodium content of 1.7 weight percent, impregnated with an aqueous solution of iron nitrate to 1.0 weight percent iron.
- Example 4 SiO_2 (Girdler T-1571) and magnetite sized to 10/30 mesh and containing 10 weight percent iron.

- Example 5 ZSM-5 base exchanged with ammonium ions and containing 0.95 weight percent potassium physically mixed with iron in the ratio of 1.03 grams TEK and 0.88 grams ZSM-5.
- Example 6 ZSM-5 having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 70, partially base exchanged with sodium and impregnated with an aqueous solution of iron nitrate to 1.0 weight percent iron.
- Example 7 Same ZSM-5 as Example 1 but physically mixed with magnetite so as to contain 1 weight percent iron.
- Example 8 Same ZSM-5 as Example 1 but impregnated with iron nitrate to 10 weight percent iron.

Conversion of syngas ($\text{H}_2/\text{CO} = 1$) was carried out over the above catalysts at 27.2-54.4 atm. gage, 288-316°C and 520-740 GHSV. The results obtained are shown in Table 2.

Table 2
SYNGAS CONVERSION TO LINEAR ALPHA OLEFINS (LAO)

Example	1	2	3	4	5	6	7	8
Catalyst Support	NaZSM-5	NaKZSM-5	Na-MOI- denite	SiO ₂	KHZSM-5	NAHZSM-5	NaZSM-5	NaZSM-5
CPI Index	0.3	0.4	9.1	6.2	63.0	11.0	0.3	0.3
Conversion, %	22	10	55	32	78	25	11.8	53.8
<u>Product Distribution, %</u>								
Methane	6.67	6.22	13.55	24.72	18.00	13.24	18.08	6.25
C ₂ + Paraffins	18.01	19.21	29.88	37.88	29.19	50.39	29.43	22.80
Linear α -olefins	48.25	67.04	37.01	16.34	4.77	5.06	26.82	45.08
Other olefins	3.18	3.82	17.14	17.48	40.56	26.59	9.34	4.58
Aromatics	-	-	-	0.76	8.48	4.71	-	-
Alcohols	13.34	3.77	2.10	2.82	-	0.01	16.33	16.67
Carbonyl Compounds	10.55	0.84	0.32	-	-	-	-	4.62
% LAO in Olefins	93.8	94.6	68.2	48.3	10.5	16.0	74.2	90.8

—
—

As can be seen from Table 2, only the catalysts of Examples 1, 2 and 8 were able significantly to enhance the product in linear alpha-olefins. Mordenite catalyst (Example 3) did not enhance the product in linear alpha-olefins as well as the catalysts of Examples 1, 2 and 8, even though its C.P.I. Index was low.

Example 7 vividly demonstrates the criticality of having the iron in the pores as evidenced by decreased linear alpha-olefins and increased methane.

Examples 4, 5 and 6 are clearly inferior. Example 8 shows that the concentration of iron is not narrowly critical.

Complete product distributions for Examples 1, 2, 3, 4, 6, 7 and 8 are shown in the following Tables.

TABLE 3
Product Distribution of Example 1

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols	Aldehydes
1	6.67	-	-	-	4.10	trace
2	1.86	-	4.66	-	4.40	trace
3	1.86	-	8.55	-	1.06	0.18
4	1.70	trace	6.12	0.50	.76	.73
5	1.34	trace	3.77	.29	.69	.81
6	1.90		3.84	.19	.66	1.28
7	1.34		3.00	.18	.51	1.32
8	1.11		2.53	.15	.37	1.25
9	.80		2.09	.27	.45	1.06
10	.71		2.04	.27	.14	1.05
11	.66		1.94	.25	.11	.81
12	.64		1.68	.18	.09	.68
13	.50		1.43	.20		.61
14	.43		1.29	.16		.39
15	.34		1.19	.16		.26
16	.56		1.01	.15		.12
17	.75		1.21	.10		
18	.49		.68	.08		
19	.45		.53	.05		
20	.37		.49			
21	.20		.20			
22	trace					
Total	24.68	trace	48.25	3.18	13.34	10.55
	Other Compounds					
	Aromatics					
	Naphthenes	0				

TABLE 5
Product Distribution of Example 3

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols	Ketones
1	13.55	-	-	-	0.46	
2	9.48	-	3.39	-	.74	
3	4.73	-	15.32	-	.10	
4	3.35	0.20	7.29	5.78	.07	
5	2.49	.23	4.05	2.46	.11	0.12
6	1.67	.18	1.95	2.72	.13	.14
7	1.91	.20	1.46	2.23	.16	
8	1.14	.12	.92	1.30	.13	
9	.84	.08	.74	.78	.07	.06
10	.56	.05	.52	.57	.05	
11	.46	.05	.39	.35	.02	
12	.48	.05	.31	.27	.01	
13	.34	.04	.26	.23		
14	.29	.03	.14	.21		
15	.26	.02	.10	.10		
16	.23	.02	.08	.10		
17	.19	.02	.06	.04		
18	.08	.01	.03			
19	.03					
20	.02					
21	.02					
22	.01					
Total	<u>42.13</u>	<u>1.30</u>	<u>37.01</u>	<u>17.14</u>	<u>2.10</u>	<u>0.32</u>
Other Compounds						
Aromatics	<u>0</u>					
Naphthenes	<u>0</u>					

TABLE 6
Product Distribution of Example 4

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols
1	24.72	-	-	-	1.48
2	9.01	-	2.72	-	1.05
3	6.84	-	10.32	-	0.29
4	3.95	-	1.77	-	trace
5	2.73	0.31	.59	6.16	
6	1.80	.53	.31	4.43	
7	1.70	.82	.13	2.93	
8	1.40	.81	.20	1.45	
9	1.04	1.06	.14	1.33	
10	.81	1.36	.22	.70	
11	.49	1.13	.21	.39	
12	.33	.84	.20	.25	
13	.26	.60	.20	.14	
14	.12	.48	.14	.14	
15	.08	.12	.03	.03	
16	.04	.06	.02	.02	
17	.02	.03	.01	.01	
18	.01	.01	trace	.01	
19	.01	trace			
20	trace				
Total	53.80	7.93	16.34	17.48	2.82
Other Compounds					
Aromatics					
Naphthenes					
<u>0.76</u>					
<u>0.87</u>					

TABLE 7
Product Distribution of Example 6

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols
1	13.24	-	-	-	0.01
2	5.88	-	2.40	-	
3	3.51	-	2.29	-	
4	3.14	-	0.37	7.79	
5	1.55	2.01	trace	7.43	
6	1.73	2.19		6.12	
7	1.74	4.46		2.89	
8	1.79	3.13		.42	
9	1.60	2.86		.47	
10	.86	2.95		.41	
11	.75	1.87		.46	
12	.33	1.44		.20	
13	.39	.80		.21	
14	.25	.96		.13	
15	.12	.57		.04	
16	.05	.31		.02	
17	.04	.17		trace	
18	.03	.16			
19	.03	.13			
20	.03	.09			
21	.03	.10			
22	.02	.09			
23	.02	.09			
24	.01	.05			
25	.02	.04			
26	.05	.06			
27	.06	.15			
28	.08	.19			
29	.07	.23			
30	.19	.22			
		.70			
Total	<u>37.61</u>	<u>26.02</u>	<u>5.06</u>	<u>26.59</u>	<u>0.01</u>
Other Compounds					
Aromatics	<u>4.71</u>				
Naphthenes	<u>0</u>				

TABLE 8
Product Distribution of Example 7

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols
1	18.08	-	-	-	2.88
2	7.47	-	4.14	-	7.06
3	4.45	-	9.16	-	2.77
4	2.98	0.20	4.35	1.40	1.27
5	1.99	.11	2.93	.36	.59
6	1.01	.47	1.37	.88	.39
7	.88	.46	1.01	.88	.33
8	.96	.44	.95	1.21	.37
9	.98	.65	.72	1.17	.36
10	.94	.65	.51	1.13	.24
11	.78	.54	.38	.83	.03
12	.64	.36	.29	.69	.02
13	.51	.26	.29	.42	.02
14	.31	.20	.23	.13	
15	.26	.07	.16	.08	
16	.21	.03	.11	.05	
17	.20	.03	.08	.03	
18	.15	.03	.07	.03	
19	.11	.02	.05	.03	
20	.05	trace	.02	trace	
21	.03				
22	trace				
Total	<u>42.99</u>	<u>4.52</u>	<u>26.82</u>	<u>9.34</u>	<u>16.33</u>
Other Compounds					
Aromatics	<u>0</u>				
Napththenes	<u>0</u>				

TABLE 9
Product Distribution of Example 8

No. C atoms	n-paraffins	Iso-paraffins	Linear α -Olefins	Other Olefins	Alcohols	Ketones
1	6.25	-	-	-	1.13	0.02
2	3.96	-	5.93	-	2.92	.14
3	2.71	-	9.60	-	1.55	.30
4	1.63	0.18	5.44	0.66	2.09	.43
5	1.13	.16	3.15	.18	2.28	.34
6	1.00	.36	2.34	.11	1.58	.35
7	.76	.14	3.09	.09	1.01	.35
8	1.09	.17	3.22	.18	.69	.35
9	.76	.18	2.85	.37	.63	1.74
10	1.09	.29	2.58	.34	.52	.18
11	1.19	.23	1.84	.47	.49	.17
12	1.18	.12	1.40	.45	.37	.15
13	1.16	.18	1.04	.43	.18	.14
14	1.02	.81	.81	.39	.08	.12
15	.85	.63	.63	.37	.01	.09
16	.73	.47	.47	.29		.07
17	.64	.35	.35	.18		.03
18	.56	.30	.30	.05		
19	.47	.10	.10			
20	.34	.04	.04			
21	.23					
22	.12					
23	.02					
24	trace					
Total	27.04	2.01	45.08	4.58	16.67	4.62
Other Compounds						
Aromatics						
Naphthenes						
0						

EXAMPLES 9-10

These Examples illustrate the use of ruthenium as the carbon oxide-reducing component. In Example 9, the same ZSM-5 zeolite having a silica-to-alumina ratio of about 1600 and a sodium content of about 1.6 wt.% as was utilized for the preparation of the catalyst of Example 1, was impregnated with an aqueous solution of ruthenium nitrate, followed by calcination overnight at 538°C and activation with flowing hydrogen at 250°C at a pressure of 34 atm.g. for two hours. This resulted in a catalyst containing 0.5 weight percent ruthenium.

The catalyst of Example 10 was prepared by subjecting silica to an aqueous impregnation with ruthenium nitrate under identical conditions to those used in preparing the catalyst of Example 9 so as to obtain a material having a ruthenium content of 0.5 weight percent on silica.

Both materials had a C.P.I. Index less than 10 and were evaluated for the conversion of syngas ($H_2/CO = 2$) at 316°C, 34 atm.g. at a GHSV of 420. The results are shown in the following Table.

TABLE 10
Effect of support on Ru catalysts

Example	9	10
Catalyst	0.5 wt.% Ru on ZSM-5	0.8 wt.% Ru on SiO ₂
Temperature, °C	316	316
Pressure, atmos. g.	34	34
GHSV, per hour	420	420
H ₂ /CO	2	2
Conversion, mole %	25.3	21.6
Product distribution, weight %		
Alcohols	6.7	10.3
Aldehydes	1.1	-
Ethers	0.4	-
Hydrocarbons	91.8	89.7
Hydrocarbon distribution, weight %		
Methane	2.8	43.4
C ₂ + Paraffins	27.1	47.9
Olefins	64.1*	8.7
	100.0	100.0

* > 95% linear alpha-olefins

From the above Table 10, it can be seen that even though both catalysts had a C.P.I. Index of less than 10, selectivity of the ZSM-5 catalyst for linear alpha-olefins is substantially higher than the silica-based catalyst. Thus, in order to obtain the desired products of this invention, it is not enough that a material be used that has a low C.P.I. Index but it must also be a ZSM-5 type zeolite in order to provide the selective conversion desired.

The Examples also demonstrate another significant advantage of the process of this invention, namely, the suppression of methane make. It should be noted that the processes of Examples 1, 2 and 8 of Table 2 and Example 9 of Table 10 involved significant suppression of methane.

Claims:

1. A process for the conversion of synthesis gas into hydrocarbons by contacting synthesis gas at an elevated temperature with a ZSM-5 type zeolite and a carbon oxide-reducing component, wherein the ZSM-5 type zeolite is substantially catalytically inert and contains the carbon oxide-reducing component within the pores thereof.
2. A process according to claim 1, wherein the hydrocarbon product is rich in linear alpha-olefins.
3. A process according to claim 2, wherein the hydrocarbon product is rich in C₄-C₆ linear alpha-olefins.
4. A process according to any one of claims 1 to 3, wherein the ZSM-5 type zeolite is ZSM-5.
5. A process according to any one of claims 1 to 4, wherein the carbon oxide-reducing component is a Fischer-Tropsch catalyst.
6. A process according to any one of claims 1 to 5, wherein the carbon oxide-reducing component is iron.
7. A process according to any one of claims 1 to 5, wherein the carbon oxide-reducing component is cobalt.
8. A process according to any one of claims 1 to 5, wherein the carbon oxide-reducing component is ruthenium.



DOCUMENTS CONSIDERED TO BE RELEVANT		CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
AP	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 102, no. 7, 26th March 1980, pages 2478-2480 Easton, U.S.A. D. FRAENKEL et al.: "Shape-selective fischer-tropsch synthesis catalyzed by zeolite-entrapped cobalt clusters"	C 07 C 1/04 B 01 J 29/30
	--	
A	ERDOL UND KOHLE - ERDGAS - PETROCHEMIE, vol. 25, April 1972, pages 187-188 Leinfelden, DE. I. ABDULAHAD et al.: "Die Fischer-Tropsch-Reaktion an zeolithischen Kobalt-, Nickel- und Eisenkontakten"	TECHNICAL FIELDS SEARCHED (Int. Cl.) C 07 C 1/04 1/02 B 01 J 29/30 29/32 29/34
	--	
A	<u>US - A - 4 172 843</u> (DWYER et al.)	
AD	<u>US - A - 4 086 262</u> (CHANG et al.)	

		CATEGORY OF CITED DOCUMENTS
		X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
		&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
The Hague	16-06-1981	VAN GEYT