United States Patent Office

2,755,228

Patented July 17, 1956

2,755,228

HYDROREFORMING EMPLOYING CARBIDE CATALYSTS

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No Drawing. Application February 25, 1952, Serial No. 273,336

8 Claims. (Cl. 196—50)

This invention relates to catalytic processes for the conversion of normally liquid hydrocarbons in the presence of hydrogen.

The more important processes that have been practiced or proposed for the catalytic conversion of hydrocarbons in the presence of hydrogen involve operating under such conditions, including pressures of about 100 to 1500 pounds per square inch and temperatures of at least 700° F., that a carbonaceous deposit forms on the catalyst, which deposit is burned off the catalyst in an oxidative regeneration period of the process. Such processes are advantageous as compared with extremely high pressure processes in which no deposit is formed on the catalyst in that equipment and operating costs (e. g. cost of compressing gases and the like) are lower and the products are improved. Processes of this type include operations wherein a relatively heavy liquid hydrocarbon or mixture of hydrocarbons such as a gas oil, whole crude, reduced crude, coke still distillate, and the like, is contacted with a catalyst in the presence of hydrogen under these elevated temperature conditions, and preferably temperatures of about 800° to 1100° F. In this type of process the hydrocarbons are subjected to hydrocracking which involves scission of carbon to carbon bonds, dehydrogenation, hydrogenation and related changes in structure of the hydrocarbons. Also, some desulfurization occurs in every case and excellent desulfurization takes place with the use of selected catalysts.

Another type of conversion process carried out in the presence of hydrogen is employed for the treatment of hydrocarbons boiling in the gasoline or naphtha boiling range and may be referred to as catalytic reforming in the presence of hydrogen or "hydroreforming." In this process the objective is primarily to accomplish isomerization and aromatization of the hydrocarbons making up the charge and consequent increase in the octane number of the product. In this type of operation there is ordinarily very little difference between the average molecular weight of the charge and that of the product although some cracking may occur, particularly under high conversion conditions. The temperature employed in catalytic reforming in the presence of hydrogen is in excess of 700° F., a temperature of about 800° to 1100° F. generally being preferred. A version of this process is generally referred to as hydroisomerization. The charge

to a hydroisomerization process is largely paraffinic and may consist of a single normal paraffin such as normal pentane or normal hexane. The principal result here is to convert the normal paraffins to isoparaffins.

As stated above, processes of these types are carried out at pressures which may vary from about 100 to about 1500 pounds per square inch. The hydrogen pressure maintained in the reaction zone has an effect upon the type of conversion taking place, other conditions being maintained constant. The maintenance of high hydrogen pressures within the indicated range is generally effective to permit conversion with longer on-stream periods. When lower hydrogen pressures within the indicated range are used, the conversion involves a more rapid formation of a carbonaceous deposit on the catalyst. Such processes, therefore, comprise a cyclic operation in which frequent regeneration is necessary.

The catalysts that have been employed for the conversion of hydrocarbons in the presence of hydrogen comprise a recognized class. These catalysts are referred to as hydrogenation catalysts and include one or more of the metals of groups V, VI, and VIII of the periodic table and the oxides of these metals. The more important of these metals are chromium, molybdenum, tungsten, cobalt and nickel. While these metals or metal oxides may be used alone, it is the usual practice to employ catalysts which comprise one or more of these metals or metal oxides deposited on a suitable support such as activated alumina, kieselguhr, silica-alumina composites containing a major proportion of silica, activated clays, and the like. A particularly valuable support is an activated alumina containing a relatively small amount of silica, for example about 5 per cent by weight, which serves to improve the surface characteristics of the support.

We have discovered in accordance with the invention that improved results can be obtained by carrying out a process for the conversion of hydrocarbons as above-described in the presence of a catalyst of the above class in which at least a part of the metal is in the form of the carbide. The carbides of these metals can be prepared by contacting the catalyst with a carbiding agent, preferably carbon monoxide, at an elevated temperature. While it is not necessary to convert all of the metal to the carbide in order to achieve the advantages of the invention, the carbiding operation should be carried out in such manner as to convert at least 25 per cent, and preferably at least 50 per cent, by weight of the metal in the catalyst to the carbide form. The metal carbides are relatively stable and will continue to be effective during a relatively long on-stream period. It is preferred in most cases to carbide the catalyst after oxidative regeneration to insure that an important part of the metal in the catalyst is in the carbide form at the beginning of the reaction period.

The effect of the carbiding treatment is in general to increase the activity of the catalyst, although the specific result of this increase in activity will vary depending upon the type of conversion operation in which the catalyst is

used, the particular catalyst employed and other factors. For example, the hydrocracking activity of a catalyst is improved by carbiding where the charge stock is a heavy hydrocarbon mixture. In hydroreforming, a higher octane product is obtained with the use of a carbided catalyst than is obtained with the use of the untreated catalyst at the same conditions. The effect of the carbiding treatment is especially noticeable when conditions adapted to result in high conversion of the charge are maintained.

In accordance with a preferred embodiment of the invention, a naphtha fraction of petroleum is subjected to hydroreforming in the presence of a carbided hydrogenation catalyst. While any of the hydrogenation catalysts are more or less satisfactory for this process, a preferred catalyst is one consisting of molybdena deposited on an activated alumina support and preferably such a support containing about 5 per cent by weight of silica. Ordinarily, the molybdena, considered to be MoO_3, constitutes about 8 to 12 per cent by weight of the finished catalyst. Depending upon the specific results that are desired to be obtained, such as the length of the process period, the pressure employed for hydroreforming may be from about 100 to about 1000 pounds per square inch. Within this pressure range the length of the on-stream period can be varied by varying the pressure and hydrogen recycle rates. When using the catalyst referred to above to obtain a high octane product, the conversion is preferably carried out at a temperature within the range of about 850° to about 950° F. These conditions result in a net production of hydrogen in the reaction zone. The hydrogen introduced into the reaction zone and formed in that zone is separated from the product and at least a part is recycled to the reaction zone. For hydroreforming the charge to the reaction zone should comprise about 1,000 to 10,000 standard cubic feet (s. c. f.) of hydrogen per barrel of naphtha charged and preferably about 1,000 to about 5,000 s. c. f.

The operating cycle for this process preferably comprises (1) carbiding the catalyst, (2) the reaction period, (3) purging the catalyst, and (4) regenerating the catalyst by burning off the carbonaceous deposit formed in the reaction period.

In carbiding by treating the catalyst with carbon monoxide, the temperature should be at least about 700° F. and preferably is between about 900° and 1200° F. With supported catalysts the temperature should be kept below about 1300° F. to avoid damage to the catalyst support. The length of time for carbon monoxide treatment is dependent upon the temperature employed and the degree of carbiding desired. The treatment should be continued until at least 25 per cent and preferably at least 50 per cent by weight of the molybdenum is in the form of the carbide. At least about 30 minutes and usually from 1 to 5 hours of treatment are required under the conditions mentioned. The carbon monoxide treatment can be carried out at any convenient pressure, for example, atmospheric pressure or somewhat higher pressures. If it is desired to avoid large pressure changes in the catalyst system during a reaction cycle, the carbon monoxide treatment can be performed at the on-stream reaction pressure, for example, between about 500 and 1000 pounds per square inch gauge. In most instances it is preferred to treat the catalyst with carbon monoxide immediately following the oxidative regeneration of the previous reaction cycle and since the temperature of the catalyst following regeneration is usually from about 1000° to 1200° F., a very satisfactory procedure is to carbide the hot regenerated catalyst with no cooling or heating between the oxidizing and carbiding phases. Following the carbiding treatment, the naphtha charge and hydrogen are contacted with the catalyst under the reaction conditions outlined above until the quality of the product falls below a selected level. The catalyst is then purged to remove occluded hydrocarbons and hydrogen and is subjected to oxidative regeneration. The regeneration is preferably accomplished by contacting the catalyst with air or another oxygen-containing gas. The regenerated catalyst is in condition for the carbiding treatment described above.

We have indicated that our preferred procedure is to carbide the catalyst without previous hydrogen reduction. However, it should be understood that the hydrogen reduction can be performed before the carbiding treatment, if so desired, and excellent results will still be obtained although we find that carbiding alone gives the best results.

The hydroreforming process as described can be carried out with the catalyst deposited in a stationary fixed bed, in which case the catalyst is usually employed in the form of granules or pellets. When using the catalyst in a fixed bed, the above cycle of operations is carried out on the catalyst in the reaction zone. Inasmuch as the reaction is endothermic, provisions are made for supplying heat to the catalyst bed during the reaction period.

This process may also be carried out utilizing the catalyst in fluidized state. In this operation a finely divided catalyst is employed. While the above cycle of operations may in this case also be carried out on the catalyst while the catalyst is in the reaction zone, it is generally preferred to provide a separate regenerator to which catalyst from the reactor may be conveyed either periodically or continuously. The regeneration may be accomplished at about the pressure in the reactor or at about atmospheric pressure. When the regeneration is carried out in a vessel separate from the reactor, the steps of reducing the catalyst with hydrogen (if hydrogen reduction is desired) and contacting the catalyst with a carbiding agent should preferably be conducted in a vessel into which the catalyst from the regenerator is introduced.

In hydroreforming processes, and especially in such processes employing a fluidized catalyst, it is advantageous to regenerate the catalyst (including burning carbonaceous deposits from the catalyst and hydrogen-reducing the oxidized catalyst) at the high pressure of the on-stream reaction so that depressuring and repressuring of the catalyst for regeneration will be unnecessary. However, steam is formed in the hydrogen reduction of an oxide catalyst, and therefore if this reduction is carried out at high pressures, the partial pressure of the steam being high, serious detrimental effects on the catalyst may be encountered. Since no steam is formed in reducing an oxidized catalyst with carbon monoxide, the reduction with carbon monoxide can be performed at high pressure with no detrimental effect on the catalyst. It is therefore an advantage of our process that the hydrogen reduction step can be eliminated and thus that the catalyst can be maintained at high pressure throughout the operating cycle of the process, with this advantage being particularly important in fluid catalyst operations.

The advantages of our procedure of carbon-monoxide treating the catalyst at substantially reaction pressure are obtainable not only in hydroreforming processes, but also in the other processes for converting hydrocarbons in the presence of hydrogen, e. g. hydrocracking and hydrodesulfurization, and especially those processes which employ a fluidized catalyst.

The following examples will further illustrate the nature of our process and will demonstrate its advantages by comparison with processes which are not performed in accordance with our invention.

EXAMPLE I

A powdered fluidizable catalyst comprising 10.78 per cent by weight molybdenum trioxide on an alumina gel base stabilized with about 5 per cent silica was calcined in air for 4 hours at 900° F. and was then fluidized in a stream of carbon monoxide at a temperature of about 1050° F. and a pressure of about 50 pounds per square inch gauge (p. s. i. g.) for a period of about 4 hours to carbide a substantial portion of the molybdenum in the catalyst. The carbon monoxide-treated catalyst was then placed on-stream to hydroreform a West Texas straight run naphtha having the characteristics listed in Table I below. The naphtha together with hydrogen was preheated to a temperature of about 900° F. before introduction to the catalytic reactor. A temperature of about 900° F., and a pressure of about 500 p. s. i. g. were maintained in the reactor throughout the on-stream period. The hydrogen concentration in the reactor was maintained at about 5140 cubic feet per barrel of liquid naphtha feed. The feed rate throughout the reaction period was maintained at about 1.0 pound of naphtha per pound of catalyst per hour. A product sample was collected for a throughput interval of 24.7 to 27.7 pounds of naphtha per pound of catalyst. Table II below records the results of the described operation in terms of yields and characteristics of the product obtained at the throughput interval indicated.

EXAMPLE II

The procedure of Example I was repeated using a molybdena catalyst of the type described but omitting the carbon monoxide treatment and subjecting the catalyst to a four hour hydrogen reduction at 900°–950° F. before placing it on-stream. Reaction conditions are listed in Table II. A sample of the product was taken for a throughput interval of 12.0 to 20.7 pounds of naphtha per pound of catalyst, and the yields and characteristics of this product are listed in Table II below.

Table I

INSPECTION OF WEST TEXAS STRAIGHT RUN NAPHTHA

Gravity, ° API	50.0
Distillation, ° F.:	
IBP	276
10%	295
50%	316
90%	342
E. P.	370
Aniline point, ° F.	108.5
Bromine No.	1.9
Sulfur, per cent (lamp)	0.256
Aromatics, per cent	14.9
Octane numbers, research:	
Clear (uncorr.)	37.5
+3 cc. TEL (uncorr.)	53.8

Table II

Example	I	II
Catalyst	CO treated	H_2 Reduced
Temperature, °F.	897	897
Pressure, p. s. i. g.	500	500
H_2 Concentration, C. F./B.	5,140	4,610
Charge Rate, Wt./Wt./Hr.	1.0	1.0
Throughput Interval, Wt./Wt.	24.7–27.7	12.0–20.7
Recovery, Wt. percent of Feed Charged:		
C_1	1.6	1.3
C_2	2.8	1.8
C_3	4.0	3.8
C_4	6.0	5.7
400° F. E. P. Gasoline (C_{5+})	84.5	88.0
Total	98.9	100.6
Recovery, Vol. Percent of Feed Charged:		
C_4	7.9	7.5
400° F. E. P. Gasoline (C_{5+})	85.0	88.5
Total	92.9	96.0
400° F. E. P. Gasoline (10 AVP—C_3 free)	95.5	101.4
Excess C_4	−2.6	−5.4
Total (100% C_4 Gasoline)	92.9	96.0
Inspection Data—Gasoline:		
Gravity, °API	53.2	52.8
Distillation, °F.—		
IBP	105	118
10%	168	194
50%	277	296
90%	337	343
E. P.	403	398
Aniline Point, °F.	82.7	96.6
Bromine No.	0.6	2.0
Sulfur, Percent (lamp)	0.012	0.011
Aromatics, Percent	38.1	30.4
Vapor Pressure, p. s. i. a.	7.2	5.7
Vapor Pressure, p. s. i. a. (Corr.—C_3 free)	5.6	4.1
Octane Numbers, Research—		
Clear (uncorr.)	79.6	71.8
+3 cc. TEL (uncorr.)	92.6	87.2
Clear (10 lbs. AVP—C_3 free)	81.0	74.5
+3 cc. TEL (10 lbs. AVP—C_3 free)	94.0	89.8

The advantages obtainable with the process of our invention are readily apparent from an examination of the data in Table II. Thus, the table shows that Example I employing the carbon monoxide-treated catalyst produced 400° F. end point gasoline (10 pounds absolute vapor pressure) having an octane number (CFRR), with 3 cc. tetraethyl lead per gallon added, of 94.0 as compared with an octane number for the corresponding product by the process of Example II of only 89.8. At such high octane number levels the differences are very significant, so that it is clear that the octane-yield relationship for our process is markedly superior to that of the process using the non-carbided catalyst (Example II).

As we have indicated, our use of carbided hydrogenation catalysts is applicable to a number of processes for conversion of normally liquid hydrocarbons in the presence of hydrogen at temperatures above about 700° F. To illustrate the practice of our invention in another such process we have conducted a series of runs in the hydrocracking of two different heavy distillate fractions employing carbon monoxide-treated hydrocracking catalysts and we have compared our results with the results obtained in hydrocracking the same stocks with untreated hydrocracking catalysts. The details of the procedure were as follows:

EXAMPLE III

A finely divided fluidizable catalyst comprising about 10 per cent by weight of mixed oxides of nickel and tungsten deposited on silica-alumina microspheres was subjected to carbon monoxide treatment as described in Example I. The carbon monoxide-treated catalyst was then employed in the fluid catalyst hydrocracking of a heavy cycle stock from thermo for catalytic cracking. Inspection data for this charge stock are given in Table III below. Reaction conditions included a temperature of about 822° F., pressure of 1,000 p. s. i. g., hydrogen concentration of 10,800 standard cubic feet per barrel of

charge, charge rate of 0.87 pound of charge per pound of catalyst per hour, and a throughput of 3.5. The results of this operation in terms of product yields and product characteristics are listed in Table III below.

EXAMPLE IV

The heavy cycle stock described in Example III was subjected to fluid catalyst hydrocracking employing a nickel-tungsten catalyst of the type described in Example III, with the exception that said catalyst was not subjected to carbon monoxide treatment, but was reduced with hydrogen before being placed on-stream. The results of the operation with the untreated catalyst in terms of product yields and characteristics are listed in Table III below.

Table III

Example		III	IV
Catalyst Treatment		Co-treated	H_2 Reduced
Temperature, ° F		822	821
Pressure, p. s. i. g		1,000	1,000
H_2 Concentration, S. C. F./B		10,800	10,450
Charge Rate, wt./wt./hr		0.87	0.93
Throughput, wt./wt		3.5	3.7
Recovery, wt. percent:			
Gas C_1-C_4		7.2	3.5
Liquid Product		86.7	96.0
Carbon			
Total		93.9	99.5
	Charge		
Inspection Data:			
Gravity, ° API	22.2	46.1	31.4
Sp. Gr	0.9212	0.7967	0.8686
Sulfur, wt. percent	0.36	0.04	0.14
Distillation—			
Percent at 392° F		58.3	19.7
Percent at 500° F		70.4	25.5
Percent at 590° F	10	82.7	42.1
Bromine No. on ovhd	9	2.9	7.9
Carbon Res. on 590° F.—			
Bttms., wt. percent	0.44	0.10	0.09

The results recorded in Table III show that the advantages of carbon monoxide treatment of hydrogenation catalysts are obtainable in the hydrocracking of a heavy cycle stock. Reference to the table shows a greatly increased conversion of the stock to gasoline boiling range product as compared with the use of the hydrogen-reduced catalyst. Thus in Example III, 58.3 per cent of the product distilled at 392° F. as compared with only 19.7 per cent for the product of Example IV. The results of Table III also indicate the excellent desulfurization obtainable with our process inasmuch as the liquid product in Example III contained only 0.04 per cent by weight sulfur as compared with 0.36 per cent by weight sulfur in the charge and 0.14 per cent by weight sulfur in the product of Example IV.

We have also conducted comparative runs on the hydrocracking of coke still distillate of Baxterville, Mississippi, crude oil using a carbon monoxide-treated catalyst in accordance with our process and using a non-carbon monoxide-treated catalyst. The procedure was as follows:

EXAMPLE IV–A

A catalyst comprising the mixed oxides of nickel and tungsten deposited in the amount of about 10 per cent by weight on a support consisting of alumina impregnated with 5 per cent silica was fluidized in a stream of carbon monoxide at 50 p. s. i. g. and 1050° F. for 3 hours to convert a substantial portion of the nickel and tungsten to their carbides. Then the Baxterville coke still distillate having the inspection data listed in Table III–A below was subjected to hydrocracking over the carbon monoxide-treated fluid catalyst under the reaction conditions listed in Table III–A. The yield and characteristics of the product obtained at a cumulative throughput of 2.0 pounds of charge per pound of catalyst are listed in Table III–A.

EXAMPLE IV–B

The Baxterville coke still distillate of Example IV–A was subjected to hydrocracking over the nickel-tungsten catalyst of Example IV–A but omitting the carbon monoxide treatment of the catalyst and reducing the catalyst with hydrogen before placing it on stream. Reaction conditions and yields and characteristics of the product obtained at a throughput of 2.1 pounds of charge per pound of catalyst are listed in Table III–A below.

Table III–A

Example		IV–A	IV–B
Catalyst Treatment		CO-treated	H_2 Reduced
Temperature, ° F		849	856
Pressure, p. s. i. g		1,000	1,000
H_2 Concentration, S. C. F./B		9,100	9,300
Charge Rate, wt./wt./hr		0.49	0.51
Throughput, wt./wt		2.0	2.1
Recovery, Wt. percent:			
Gas C_1-C_2		9.6	6.6
Liquid Product		86.8	91.4
Sulfur		1.8	1.8
Carbon		1.8	1.5
Total		100.0	101.3
	Charge		
Inspection Data:			
Gravity, ° API	27.0	47.2	45.2
Sp. Gr	0.8927	0.7927	0.8008
Sulfur, wt. percent	1.86	0.03	0.06
Distillation—			
Percent at 392° F	11.0	60.1	54.5
Percent at 500° F	21.0	83.2	76.5
Percent at 590° F	36.0	94.4	89.8
Bromine No. Ovhd		4.2	4.4
Carbon Res. on 590° F.—			
Bttms, wt. percent	1.3	0.11	0.12

Table III–A shows that the product of Example IV–A had greater proportions of all fractions boiling below 590° F. than the product obtained in Example IV–B and the gravity of the product was 47.2° API as compared with 45.2° API for the product obtained with the untreated catalyst. The total yield of product for Example IV–A was of course somewhat less than for Example IV–B but was by no means so much less as to offset the fact that it was a much more valuable product. It is clear from the results of Examples III, IV, IV–A and IV–B that our carbiding treatment offers great advantages in hydrocracking processes. These are processes which, as the tables show, are operated at somewhat higher pressures and lower temperatures than hydroreforming processes and in which the charge is a hydrocarbon oil heavier than gasoline, e. g. stocks of the gas oil range or heavier. Typical ranges of operating conditions for such processes are: temperature, 750–950° F.; pressure, 500–1500 pounds per square inch gauge; hydrogen concentration, 2,500–30,000 standard cubic feet per barrel of oil; and charge rate of 0.25–3.0 pounds of oil per pound of catalyst per hour.

In order to demonstrate the effect of variations in reaction temperature in hydroreforming with a carbon monoxide-treated catalyst, we have conducted a series of runs at different temperatures.

EXAMPLE V

The West Texas naphtha described in Table I was hydroreformed at a temperature of about 875° F. substantially in accordance with the procedure of Example I. Samples of products for throughput intervals of 12.2 to 20.1 and 49.7 to 57.4 were taken and the data concerning yields and characteristics of these products are given in Table IV below.

EXAMPLE VI

The procedure of Example V was repeated using a reaction temperature of about 900° F. and collecting the prod-

uct for throughput intervals of 11.7 to 19.8 and 50.8 to 58.8, the characteristics of which are given in Table IV below.

EXAMPLE VII

The procedure of Example V was repeated using a reaction temperature of about 925° F. and collecting the product for throughput intervals of 11.5 to 19.5 and 51.2 to 59.4, the characteristics of which are given in Table IV below.

Table IV

HYDROREFORMING WEST TEXAS NAPHTHA OVER CO TREATED MOLYBDENA CATALYST

Example No.	V		VI		VII	
Temperature, ° F	874	875	900	901	927	925
Pressure, p. s. i. g.	500	500	500	500	500	500
H_2 Concentration, C. F./B.	5,000	5,000	4,740	4,750	4,760	4,600
Charge Rate, Wt./Wt./Hr.	0.99	0.97	1.0	1.0	1.0	1.0
Throughput Interval, Wt./Wt.	12.2-20.1	49.7-57.4	11.7-19.8	50.8-58.8	11.5-19.5	51.2-59.4
Recovery, Wt. Percent of Feed Charged:						
C_1	0.9	0.9	1.7	1.6	3.0	2.4
C_2	1.7	1.8	3.0	2.5	4.4	3.6
C_3	3.1	3.8	6.0	4.6	7.5	6.3
C_4	5.1	5.8	8.1	7.4	10.0	8.5
400° F. E. P. Gasoline (C_{5+})	87.8	85.2	78.1	78.8	70.6	74.8
Total	98.6	97.5	96.9	94.9	95.5	95.6
Recovery Vol. Percent of Feed Charged:						
C_4	6.7	7.7	10.7	9.8	13.2	11.2
400° F. E. P. Gasoline (C_{5+})	88.4	85.7	78.4	78.8	70.4	74.4
Total	95.1	93.4	89.1	88.6	83.6	85.6
400° F. E. P. Gasoline (10 AVP—C_3 free)	100.7	99.4	88.0	89.0	81.3	84.7
Excess C_4	−5.6	−6.0	+1.1	−0.4	+2.3	+0.9
Total (100% C_4)	95.1	93.4	89.1	88.6	83.6	85.6
Inspection Data—Total Product (As Produced):						
Gravity, ° API	52.8	52.9	52.7	52.6	52.1	51.6
Sp. Gr.	0.7678	0.7674	0.7682	0.7686	0.7707	0.7728
Distillation °F.—						
IBP	101	103	98	124	109	108
10%	185	193	162	182	146	151
50%	292	292	278	276	257	270
90%	339	343	341	330	336	336
E. P.	388	393	400	392	411	409
Total Aromatics, Percent	28.6	35.5	38.1	38.1	46.8	42.1
Olefins, Percent	1.6	1.2	1.4	1.4	1.2	1.9
Aniline Point, °F.	99.9	96.1	79.9	81.8	57.4	69.3
Bromine No.	2.1	1.6	1.9	1.9	1.7	2.6
Sulfur, Wt. Percent	0.014	0.018	0.014	0.012	0.021	0.014
Vapor Pressure, p. s. i. a.	5.4	4.5	7.3	7.1	6.7	7.7
Vapor Pressure, p. s. i. a. (Corr.—C_3 free)	3.7	2.8	6.1	5.9	5.5	5.6
Octane Numbers, Research—						
Clear (Uncorr.)	69.4	72.0	81.1	80.0	89.8	84.6
+3 cc. TEL (uncorr.)	85.6	87.8	93.3	92.8	97.9	95.2
Clear (10 lbs. AVP—C_3 free)	72.3	75.1	82.3	81.3	90.5	85.7
+3 cc. TEL (10 lbs. AVP—C_3 free)	88.2	90.5	94.6	94.1	99.0	96.5

The results of Table IV indicate excellent yield-octane relationships for all three temperatures employed. In general, however, for production of automobile fuels the yield-octane relationship of the 900° F. run (Example VI) would be the most favorable. In this run, as can be seen from the table, at a throughput interval of 11.7 to 19.8 the yield of 400° F. end point gasoline (10 lb. AVP3) was 88.0 per cent and this product had a leaded octane number (CFRR) of 94.6, while at a throughput interval of 50.8 to 58.8 the yield of the same gasoline was 89.0 volume per cent with an octane rating of 94.1. These results are even more favorable when the fact is considered that the total recovery for each period was low, namely 96.9 weight per cent of the feed charged for the first period of this run and 94.9 weight per cent for the second period. Another outstanding fact which is observable in the results of these three runs is the continuing high activity of the carbon monoxide-treated catalyst throughout the on-stream period. Thus, in all three runs the octane ratings of product at high throughputs were substantially as good as or better than the octane ratings at low cumulative throughputs. Since the West Texas naphtha feed contained 0.256 per cent by weight sulfur, it is evident that the carbon monoxide-treated catalyst is not inactivated by sulfur over a long reaction period.

We have conducted a series of runs to demonstrate the superiority of our process of hydroreforming with a carbon monoxide-treated catalyst as compared with hydroreforming with an unreduced catalyst or with a catalyst which is treated with a mixture of carbon monoxide and hydrogen. The runs were conducted as follows:

EXAMPLE VIII

The molybdena on alumina fluidized catalyst described in Example I was calcined by heating in air for 4 hours at 900° F. and then contacted with a stream of carbon monoxide at a pressure of 50 pounds per square inch gauge and a temperature of 1050° F. for 3 hours. The treated catalyst was then placed on stream for hydroreforming the West Texas naphtha of Table I. The reaction conditions included a temperature of about 850° F. and a pressure of 500 p. s. i. g. Product samples were taken for throughput intervals of 13.8 to 21.0 and 53.7 to 62.6. Table V below lists the reaction conditions and the yields and characteristics of the product samples taken.

EXAMPLE IX

The catalyst of Example I was calcined in air at 900° F. for 4 hours and then contacted with a nitrogen stream for 3 hours at 1050° F. and 50 p. s. i. g., following which the catalyst was placed on stream for hydroreforming the naphtha of Table I under reaction conditions substantially the same as those of Example VIII. Product samples were taken for throughput intervals of 12.1 to 20.6 and 54.3 to 60.2. Table V below lists the yields and characteristics of the product samples.

EXAMPLE X

The catalyst of Example I was calcined as in Examples VIII and IX and was then contacted with a stream of carbon monoxide and hydrogen (mixed in 1:1 mol ratio) at 1050° F. and 50 p. s. i. g. for 3 hours, following which the catalyst was placed on stream for hydroreforming the naphtha of Table I under substantially the same reaction conditions as Examples VIII and IX. Product samples were taken for throughput intervals of 11.8 to 19.9 and 51.5 to 59.5 and the yields and characteristics of these products are listed in Table V below.

Table V

Example No.	VIII		IX		X	
Temperature, °F	844	852	850	849	848	851
Pressure, p. s. i. g.	500	500	500	500	500	500
H_2 Concentration, C. F./B.	4,880	4,600	4,640	4,730	4,920	4,900
(Charge Rate), Wt./Wt./Hr.	1.1	1.1	1.1	0.98	1.0	1.0
Throughput Interval, Wt./Wt.	13.8–21.0	53.7–62.6	12.1–20.6	54.3–60.2	11.8–19.9	51.5–59.5
Catalyst Conditioning	CO-treated		N_2-treated		CO+H_2-treated	
Recovery, Wt.% of Feed Charged:						
C_1	2.2	0.9	0.6	0.6	0.7	0.7
C_2	3.0	1.5	1.2	1.0	0.8	1.1
C_3	5.2	3.1	2.2	2.8	2.4	2.8
C_4	7.0	4.7	2.6	3.4	3.5	3.4
400° F. E. P. Gasoline (C_{5+})	77.6	85.8	90.7	93.6	91.4	88.9
Total	95.0	96.0	97.3	101.4	98.8	96.9
Recovery, Vol. Percent of Feed Charged:						
C_4	9.3	6.2	3.4	4.5	4.6	4.5
400° F. E. P. Gasoline (C_{5+})	77.6	86.4	90.1	94.0	92.6	89.3
Total	86.9	92.6	93.5	98.5	97.2	93.8
400° F. E. P. Gasoline (10 AVP—C_3 free)	85.5	96.5	101.3	105.3	103.9	100.0
Excess C_4	1.4	−3.9	−7.8	−6.8	−6.7	−6.2
Total (100% C_4 Gasoline)	86.9	92.6	93.5	98.5	97.2	93.8
Inspection Data—Total Product (as produced):						
Gravity, °API	52.5	52.9	51.9	52.0	53.4	52.4
Sp. Gr.	0.7690	0.7674	0.7715	0.7711	0.7653	0.7694
Distillation, °F—IBP	101	110	126	115	107	110
10%	150	192	249	235	198	205
50%	272	295	305	305	295	299
90%	340	339	340	342	338	342
E. P.	425	391	378	383	380	388
Total Aromatics, Percent	41.1	27.7	22.7	24.0	24.4	25.5
Aniline Point, ° F	68.7	99.9	113.0	109.4	107.0	104.8
Bromine No.	3.3	2.6	2.2	2.1	2.1	3.1
Sulfur, Wt. Percent	0.012	0.012	0.018	0.014	0.023	0.010
Vapor Pressure, p. s. i. a.	8.8	6.3	5.4	4.6	5.4	5.5
Vapor Pressure, p. s. i. a. (corr.—C_3 free)	7.6	5.1	4.2	3.8	4.2	4.7
Octane Numbers, Research—						
Clear	85.0	68.5	57.8	60.0	64.8	64.7
+3 cc. TEL	94.3	85.2	77.6	79.5	82.2	82.4
Clear (10 lbs. AVP—C_3 free)	85.6	70.9	61.4	63.7	67.9	67.4
+3 cc. TEL (10 lbs. AVP—C_3 free)	95.1	87.3	80.7	82.6	84.9	84.9

The results of Example VIII listed in Table V again show the excellent results obtainable with the process of our invention. Thus in Example VIII at a throughput interval of 13.8 to 21.0 the yield of 400° F. end point gasoline (10 lb. AVP) was 85.5 volume per cent of the feed and had a leaded octane rating (CFRR) of 95.1 and at a throughput interval of 53.7 to 62.6 the yield of the same product was 96.5 volume per cent and the octane rating was 87.3. It should be observed also that the temperature in this run was only about 850° F., which is not generally the optimum temperature for hydroreforming this particular naphtha by our process. The results of Example IX show that hydroreforming with the unreduced catalyst (nitrogen-treated) is markedly inferior to our process because of the very low octane ratings of the product. Thus the leaded octane ratings of the 10 lb. AVP gasoline for the two periods of Example IX which are recorded were only 80.7 and 82.6. The results of Example X establish the fact that treating the catalyst with a mixture of carbon monoxide and hydrogen is not equivalent to our process of treating the catalyst with pure carbon monoxide. Thus for substantially equal throughputs the leaded octane ratings of the products of Example X were only 84.9 for both periods as compared with 95.1 and 87.3 for the similar periods of our process.

We have conducted runs to compare the hydroreforming results of a catalyst which is carbon monoxide treated according to our process, with those of a catalyst which is both hydrogen reduced and carbon monoxide treated. The procedure in obtaining the latter results was as follows:

EXAMPLE XI

The molybdena on alumina fluid catalyst previously described was calcined in air for four hours at 900° F., then hydrogen reduced for four hours at 900° F. and finally carbon monoxide treated for three hours at 900° F. The catalyst was then placed on stream for hydroreforming the West Texas naphtha of Table I under the reaction conditions listed in Table VI. Product samples were taken during throughput intervals of 12 to 21.6 and 33 to 41.2. The yields and characteristics of these products are listed in Table VI.

Table VI

Example No.	XI	
Temperature, ° F	902	900
Pressure, p. s. i. g.	500	500
H_2 Concentration, C. F./B.	4,170	4,150
Charge Rate, Wt./Wt./Hr.	1.0	1.0
Throughput Interval, Wt./Wt.	12–21.6	33–41.2
Recovery, Wt. Percent of Feed Charged:		
C_1	2.2	1.2
C_2	2.1	1.8
C_3	3.5	4.7
C_4	5.0	5.7
400° F. E. P. Gasoline (C_{5+})	82.5	82.9
Total	95.3	96.3
Recovery, Vol. Percent of Feed Charged:		
C_4	5.6	7.5
400° F. E. P. Gasoline (C_{5+})	82.6	83.0
Total	89.2	90.5
400° F. E. P. Gasoline (10 lb. AVP—C_3 free)	93.2	93.3
Excess C_4	−4.0	−2.8
Total (100% C_4 Gasoline)	89.2	90.5
Inspection Data—Total Product (as produced):		
Gravity, ° API	52.8	52.2
Sp. Gr.	0.7690	0.7703
Sulfur, Wt. Percent	0.019	0.013
Olefins, Percent by Vol.	1.0	1.2
Bromine No.	1.3	1.6
Aniline Point, ° F.	84.9	86.4
Aromatic Content, Percent by Vol.	36.0	35.5
Octane Numbers, Research—		
Clear	78.5	77.6
+3 cc. TEL	90.4	90.6
Clear (10 lbs. AVP—C_3 free)	80.0	79.2
+3 cc. TEL (10 lb. AVP—C_3 free)	92.0	92.3
Vapor Pressure, AVP lb.	7.1	6.4
Vapor Pressure, AVP (Corr.—C_3 free)	5.9	5.6
Distillation, Naphtha—		
Over Point, ° F.	107	109
End	397	394
10% at ° F.	165	176
50%	280	284
90%	337	339
Recovery, Percent	98.5	97.0
Residue, Percent	1.2	1.1
Loss, Percent	0.3	1.9

The results of Example XI which are recorded in Table VI should be compared with the results of Example VI in Table IV in order to see the differences in effect of our preferred procedure of conditioning the catalyst by carbiding alone and the procedure of conditioning the catalyst by first reducing it with hydrogen and then carbiding. Thus the leaded octane ratings (CFRR) of the 400° F. end point gasoline (10 lbs. AVP) were 94.6 and 94.1 for the two product samples of Example VI and only 92.0 and 92.3 for the two corresponding samples of the Example XI product. These differences are, of course, very important for such high octane numbers, and show clearly that our preferred procedure of carbiding without a prereduction of the catalyst gives better results than reducing the catalyst and then carbiding. Table VI, however, shows that the excellent desulfurization results of our process which can be seen in all of the previous data discussed are obtainable even though the carbiding of the catalyst is preceded by hydrogen reduction.

To illustrate the application of our process to the hydroreforming of an additional naphtha stock, we have hydroreformed an Eastern Venezuela naphtha over a carbon monoxide-treated catalyst in the manner described in Example XIII.

EXAMPLE XII

The molybdena-on-alumina fluid catalyst previously described was calcined and then carbon monoxide-treated for 3 hours at 1050° F. and 50 p. s. i. g. The carbon monoxide-treated catalyst was then placed on stream to hydroreform an Eastern Venezuela naphtha having a boiling range of 288° to 395° F., a sulfur content of 0.023 weight per cent and a research octane number with 3 cc. per gallon of TEL added of 67.6. The hydroreforming conditions included a pressure of 500 p. s. i. g., a hydrogen concentration of about 5000 cubic feet per barrel of naphtha, a charge rate of 1.0 wt./wt./hr., a temperature of 851° F. for the throughput interval of 5.1 to 10.1 pounds of naphtha per pound of catalyst, a temperature of 877° F. for the throughput interval of 15.2 to 20.3 and a temperature of 901° F. for the throughput interval of 25.5 to 30.6. Product samples were taken for the three indicated intervals. The product for the throughput interval of 5.1 to 10.1 showed a yield of 96.6 volume per cent 400° F. end point gasoline (10 lbs. AVP) having a research octane number leaded of 94.4. At throughput intervals of 15.2 to 20.3 and 25.5 to 30.6 the yields of similar material were 100.7 per cent and 91.4 per cent respectively having research octane numbers leaded of 94.7 and 96.1 respectively. The sulfur contents of the three product samples were 0.004 per cent, 0.007 per cent, and 0.006 per cent.

The results of Example XII show high yields of very high octane gasoline with sustained high catalyst activity throughout the reaction period. Desulfurization throughout the reaction period was excellent.

It will be understood that the foregoing examples are merely illustrative of the invention and that comparable results can be obtained by using carbided hydrogenation catalysts in other processes for the conversion of hydrocarbons in the presence of hydrogen.

Because carbon monoxide is readily available and easy to use, it is the preferred carbiding agent. However, any of the usual carbiding agents can be used, for example hydrocarbons such as paraffinic or olefinic gases but in many cases higher carbiding temperatures or longer periods of treatment are required to obtain the same conversion of the material to the carbided form if other agents are used.

With respect to the hydrogen concentration that should be employed in the present process, it will be understood that the optimum concentration in each case will vary depending upon the particular operation being carried out, but there must be sufficient hydrogen to make the operation what might be termed a hydroconversion process. Thus, the hydrogen concentration should be about 1,000 to 30,000 standard cubic feet of hydrogen per barrel (42 U. S. gallons) of charge hydrocarbons.

Obviously many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the conversion of normally liquid hydrocarbons which comprises contacting said hydrocarbons under conversion conditions including a temperature of at least 700° F., a pressure of between about 100 and 1500 pounds per square inch, and a hydrogen concentration of about 1000 to 30,000 standard cubic feet of hydrogen per barrel of said hydrocarbons with a hydrogenation catalyst comprising a metal selected from the group consisting of molybdenum, tungsten and nickel in which at least part of the metal is in the form of the carbide.

2. A naphtha hydroreforming process which comprises contacting naphtha under hydroreforming conditions including a temperature of at least 700° F., a pressure of between about 100 and 1000 pounds per square inch, and a hydrogen concentration of 1,000 to 10,000 standard cubic feet of hydrogen per barrel of said naphtha with a supported molybdenum hydrogenation catalyst in which at least part of the molybdenum is in the form of the carbide.

3. A process in accordance with claim 2 in which said hydrogenation catalyst consists of a molybdenum catalyst supported on activated alumina.

4. A process for hydroreforming naphtha which comprises contacting said naphtha under hydroreforming conditions including temperature of about 850° to 950° F., pressure between about 100 and 1000 pounds per square inch, and hydrogen concentration of about 1000 to 10,000 standard cubic feet of hydrogen per barrel of said naphtha with a molybdenum catalyst supported on activated alumina in which at least 25 per cent by weight of the molybdenum is in the form of the carbide.

5. A process for the conversion of normally liquid hydrocarbons which comprises contacting said hydrocarbons under conversion conditions including temperature of at least 700° F., pressure between about 100 and 1500 pounds per square inch and hydrogen concentration of about 1000 to 30,000 standard cubic feet of hydrogen per barrel of said hydrocarbons with a precarbided hydrogenation catalyst comprising a metal selected from the group consisting of molybdenum, tungsten and nickel, said catalyst having been precarbided by separately contacting it with carbon monoxide at a temperature of about 700° to 1200° F. until at least 25 per cent by weight of said metal is in the form of the carbide.

6. A process for hydroreforming naphtha which comprises contacting said naphtha under hydroreforming conditions including temperature of about 800° to 1100° F., pressure of about 100 to 1000 pounds per square inch and hydrogen concentration of about 1000 to 10,000 standard cubic feet of hydrogen per barrel of said hydrocarbons with a precarbided molybdenum catalyst supported on activated alumina, said catalyst having been precarbided by separately contacting it with carbon monoxide at temperature of about 900° to about 1000° F. for about one to five hours.

7. A process for the conversion of normally liquid hydrocarbons which comprises contacting a hydrogenation catalyst metal selected from the group consisting of molybdenum, tungsten and nickel with carbon monoxide at a temperature above about 900° F., and a pressure of between about 100 and 1500 pounds per square inch for at least about 30 minutes, thereafter contacting said catalyst with said hydrocarbons at a temperature above about 700° F., a hydrogen concentration of 1000 to 30,000 standard cubic feet of hydrogen per barrel of said liquid

hydrocarbons, and at substantially the pressure employed in contacting said catalyst with carbon monoxide.

8. A hydrocracking process which comprises contacting hydrocarbons boiling above the gasoline range under conversion conditions including a temperature of between about 750° and 900° F., a pressure of between about 500 and 1500 pounds per square inch, and a hydrogen concentration of 2500 to 30,000 standard cubic feet of hydrogen per barrel of liquid hydrocarbons with a supported hydrogenation catalyst comprising a metal selected from the group consisting of molybdenum, tungsten and nickel in which at least about 25 per cent of the metal is in the form of a carbide.

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