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(54) CONVERSION OF SYNTHESIS GAS TO HYDROCARBON MIXTURES

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Processes for the conversion of gaseous mixtures comprising hydrogen and carbon monoxide are known in the prior art. Also various processes may be employed for the preparation of such gases. Those of major importance depend either on the partial combustion of fuel with an oxygen containing gas or on the high temperature reaction of a selected fuel with steam, or on a combination of those two reactions. It is known that synthesis gas will undergo conversion reactions to form reduction products of carbon monoxide, such as hydrocarbons, at temperatures in the range of 300°F to about 850°F, at pressures in the range of one atmosphere up to about 1000 atmospheres in the presence of a fairly wide variety of catalysts. The Fischer-Tropsch process for example, produces a range of liquid hydrocarbons, a portion of which have been used as relatively low octane gasoline materials. Catalyst employed in this process and some related processes include those based on metals and/or oxides of iron, cobalt, nickel, ruthenium, thorium, rhodium and osmium. On the other hand, the Fischer-Tropsch processing technology has been plagued with numerous problems such as deactivation of the catalyst with sulfur and catalyst regeneration problems. In addition it has been difficult to find and identify those conditions which produce liquid hydrocarbons boiling in the gasoline boiling range containing highly branched paraffins and substantial quantities of aromatic hydrocarbons required to produce high quality gasoline. A number of publications review the status of the Fischer-Tropsch synthesis art. None of these publications however provide a satisfactory answer for processing synthesis gas to hydrocarbons including those boiling in the gasoline boiling range where the catalyst is subjected to continuous or intermittent contact with sulfur.

The present invention is concerned with a recently discovered and unexpected method for converting synthesis gas to desired hydrocarbon products including gasoline boiling range aromatics in the presence of sulfur.

It has now been discovered that synthesis gas with or without sulfur such as hydrogen sulfide present may be converted to hydrocarbons by contacting the synthesis gas with a special catalyst composition which is relatively insensitive to sulfur and whose activity and selectivity may even be improved as well as restored after continuous exposure to sulfur in the synthesis gas feed. The present invention is concerned with the catalytic conversion of synthesis gas to desired hydrocarbon products including gasoline boiling range aromatics wherein the catalyst is continuously or intermittently subjected either by design or by accident to contact with sulfur components in the synthesis gas. In a particular respect the present invention is concerned with the conversion of synthesis gas comprising hydrogen and carbon monoxide derived, for example, from coal with or without the presence of sulfur therein to form paraffin and aromatic hydrocarbons preferably boiling within the gasoline boiling range by contacting the syngas with a particular heterogeneous catalyst mixture relatively insensitive to sulfur compounds. More particularly the present invention is concerned with the conversion of synthesis gas comprising carbon monoxide and hydrogen to hydrocarbon products by contacting a special class of crystalline zeolites represented by ZSM—5 in admixture with a carbon monoxide reducing component comprising hafnium and/or zirconium, as metal, oxide and/or sulfide. Molybdenum may be present in admixture therewith.

The synthesis gas may be prepared from fossil fuels by any one of the methods known in the prior art including in situ gasification processes such as underground combustion of coal and petroleum deposits. The term fossil fuels is intended to include anthracite and bituminous coal, lignite, crude petroleum, shale oil, oil from tar sands, natural gas, as well as fuels derived by separation or transformation of these materials.

The synthesis gas produced from fossil fuels will often contain various impurities such as particulates, sulfur, and metal carbonyl compounds and will be characterized by a hydrogen to carbon oxides (carbon monoxide and carbon dioxide) ratio which will depend on the fossil fuel and the particular gasification technology utilized. In general, it has been essential heretofore to purify the raw synthesis gas for the removal of these impurities. It has now been found however that sulfur in the syngas (synthesis gas) need not be removed when the catalysts of this invention are employed to effect conversion of the synthesis gas. However, it may be desirable under some conditions to effect a partial removal of the sulfur and complete removal of other undesired contaminants. In the conversion operations of this invention, it is preferred to adjust the hydrogen to carbon oxides volume ratio to be within the range of from 0.2 to 6.0 and more usually adjusted to a 1/1 ratio prior to contact with the catalyst. The well known water gas shift reaction may be used to increase the hydrogen ratio if required or in the event of a hydrogen rich synthesis gas, it may be adjusted by the addition of carbon monoxide and/or carbon dioxide.

The heterogeneous catalyst mixture of this invention is one comprising at least two components intimately mixed with one another and known and referred to as a sulfur insensitive or sulfur tolerant catalyst mixture. The sulfur tolerant component may or may not lose some activity in the presence of sulfur but at least it will reactivate itself substantially completely simply by removing or reducing the presence of sulfur in the syngas feed. Thus in the process of this invention it is particularly contemplated employing a catalyst mixture in which the carbon monoxide reducing component is selected from a class of inorganic substances that are substantially sulfur insensitive by having activity for the reduction of carbon monoxide in the presence of hydrogen to form hydrocarbons and in which the other component is a zeolite selected from a particular class of crystalline aluminosilicate characterized by a pore dimension greater than about 5 Angstroms, a silica to alumina ratio greater than 12, and a constraint index in the range of 1 to 12. The class of crystalline zeolite so classified and identified herein is a class of crystalline zeolites represented by ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38.

Known Fischer-Tropsch synthesis catalysts other than thoria have been found to be substantially completely deactivated by contact with sulfur or compounds of sulfur thereby requiring their removal from the process since a satisfactory regeneration procedure has not been found that will restore the sulfur deactivated catalyst activity and selectivity. The inorganic substance may be employed in amounts ranging from 0.1 per cent up to 80 per cent by weight and preferably is less than 60 per cent by weight of the active components of the intimate mixture. Most preferably the catalyst admixture comprises a volume excess of crystalline aluminosilicate in relation to carbon monoxide reducing catalyst.

The acidic crystalline aluminosilicate component of the heterogeneous catalyst is characterized by a pore dimension greater than about 5 Angstroms, i.e., it is capable of sorbing paraffins having a single methyl branch as well as normal paraffins, and it has a silica-to-alumina ratio of at least 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 catalysts referred to herein utilize members of a special class of zeolites exhibiting some unusual properties. These zeolites induce profound transformations of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields and are generally highly effective in alkylation, isomerization, disproportionation and other reactions involving aromatic hydrocarbons. Although they have unusually low alumina contents, i.e. high silica to alumina ratios, 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 dimensino 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 type B catalysts in this invention possess, in combination: a silica to alumina ratio of at least 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 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 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 twelve-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 1000°F for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 550°F and 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 is an inclusive rather than an exclusive value. That is, a zeolite when tested by any combination of conditions within the testing definition set forth herein above 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-21, and other similar materials. Recently issued U.S. Patent 3,702,886 describes ZSM-5. ZSM-11 is more particularly described in U.S. Patent 3,709,979. ZSM-12 is more particularly described in U.S. Patent 3,832,449.

French Specification 74-12078 describes zeolite composition, and methods of making such, designated as ZSM-21 which are useful in this invention.

The specific zeolites described, when prepared in the presence of organic cations, are substantially catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000°F for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this special type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type zeolite by base exchange with ammonium salts followed by calcination in air at about 1000°F for from 15 minutes to 24 hours.

Natural zeolites may sometimes be converted to this type zeolite by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, alone or in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12 and ZSM-21, with ZSM-5 particularly preferred.

The zeolites used as catalysts in this invention may be in the hydrogen form or they may be base exchanged or impregnated to contain ammonium or a metal cation complement. It is desirable to calcine the zeolite after base exchange. The metal cations that may be present include any of the cations of the metals of Groups I through VIII of the periodic table. However, in the case of Group IA metals, the cation content should in no case be so large as to substantially eliminate the activity of the zeolite for the catalysis being employed in the instant invention. For example, a completely sodium exchanged H-ZSM-5 appears to be largely inactive for shape selective conversions required in the present invention.

In a preferred aspect of this invention, the zeolites useful as catalysts herein are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred catalysts of this invention are those comprising zeolite having a constraint index as defined above of 1 to 12, a silica to alumina ratio of at least 12 and a dried crystal density of not substantially less than 1.6 gram per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference Molecular Sieves, London, April, 1967", published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pyknometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density of course must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, seems to be important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites including some which are not within the purview of this invention are:

Zeolite	Void Volume	Framework Density
Ferrierite	0.28 cc/cc	1.76 g/cc
Mordenite	.28	1.7
ZSM-5, -11	.29	1.79
Dachiardite	.32	1.72
L	.32	1.61
Clinoptilolite	.34	1.71
Laumontite	.34	1.77
ZSM-4 (Omega)	.38	1.65
Heulandite	.39	1.69
P	.41	1.57
Offretite	.40	1.55
Levynite	.40	1.54
Erionite	.35	1.51
Gmelinite	.44	1.46
Chabazite	.47	1.45
A	.5	1.3
Y	.48	1.27

The heterogeneous catalysts may be prepared in various ways. The two components may be separately prepared in the form of catalyst particles such as pellets or extrudates, for example, and simply mixed in the required proportions. The particle size of the individual component particles may be quite small, for example, from 20 to 150 microns, when intended for use in fluid bed operation; or they may be as large as up to about ½ inch for fixed bed operation. Or, the two components may be mixed as powders and formed into pellets or extrudate, each pellet containing both components in substantially the required proportions. Binders such as clays may be added to the mixture. Alternatively, the component that has catalytic activity for the reduction of carbon monoxide may be formed on the acidic crystalline aluminosilicate component by conventional means such as impregnation of that solid with salt solutions of the desired metals, followed by drying and calcination. Base exchange of the acidic crystalline aluminosilicate component also may be used in some selected cases to effect the introduction of part or all of the carbon monoxide reduction component. Other means for forming the intimate mixture may be used, such as: precipitation of the carbon monoxide reduction component in the presence of the acidic crystalline aluminosilicate; or electroless deposition of metal on the zeolite; or deposition of metal from the vapor phase. Various combinations of the above preparative methods will be obvious to those skilled in the art of catalyst preparation. It should be cautioned, however, to avoid techniques likely to reduce the crystallinity of the acidic crystalline aluminosilicate.

It will be recognized from the foregoing description that the heterogeneous catalysts, i.e., the above-described intimate mixtures, used in the process of this invention, may have varying degrees of intimacy. At one extreme, when using ½ inch pellets of the carbon monoxide reducing component mixed with ½ inch pellets of the acidic crystalline aluminosilicate, substantially all locations within at least one of the components will be within not more than about ½ inch of some of the other component, regardless of the proportions in which the two components are used. With different sized pellets, e.g., $\frac{1}{2}$ inch and $\frac{1}{4}$ inch, again substantially all locations within at least one of the components will be within not more than about $\frac{1}{2}$ inch of the other component. These examples illustrate the lower end of the degree of intimacy required for the practice of this invention. At the other extreme, one may ball mill together acid crystalline aluminosilicate particles of about 0.1 micron particle size with colloidal zinc oxide of similar particle size followed by pelletization. for this case, substantially all the locations within at least one of the components will be within not more than about 0.1 micron of some of the other component. This exemplifies about the highest degree of intimacy that is practical. The degree of intimacy of the physical mixture may also be expressed as the minimum distance of separation of the central points located within the particles of the two components. This will, on average, be represented by one-half the sum of the average particle size for the two components. Thus, for the foregoing example illustrating the highest degree of intimacy, the centers of the particles of either of the two components will be separated from the nearest particle of the other component by an average distance of at least about 0.1 micron. The degree of intimacy of the heterogeneous catalyst is largely determined by its method of preparation, but it may be independently verified by physical methods such as visual observations, examination in an ordinary microscope or with an electron microscope, or by electron microprobe analysis.

In the process of this invention, synthesis gas is contacted with the heterogeneous catalyst at a temperature in the range of from 400°F to 1000°F, preferably from 500°F to 850°F, at a pressure in the range of from 1 to 1000 atmospheres, preferably from 3 to 200 atmospheres, and at a volume hourly space velocity in the range of from 500 to 50,000 volumes of gas, at standard temperature and pressure per volume of catalyst, or equivalent contact time if a fluidized bed is used. The heterogeneous catalyst may be contained as a fixed bed, or a fluidized bed may be used. The product stream containing hydrocarbons, unreacted gases and steam may be cooled and the hydrocarbons recovered by any of the techniques known in the art, which techniques do not constitute part of this invention. The recovered hydrocarbons may be further separated by distillation or other means to recover one or more products such as high octane gasoline, propane fuel, benzene, toluene, xylenes, or other aromatic hydrocarbons.

The following Examples are given for the purpose of illustrating the invention; the percentages are by weight.

Example 1.

A sample of pure ZrO_2 was made by thermal decomposition of the oxalate thereof. Composite catalysts were made by ball-milling and pelleting.

Synthesis gas ($H_2/CO = 1$) was reacted over zirconia and a zirconia-ZSM-5 crystalline zeolite composite catalyst at 1200 psig, 800°F and 1.3—1.5 VHSV (gas at standard temperature and pressure) (based on ZrO_2)or 720—750 VHSV (based on total reaction volume). The effect of the ZSM-5 crystalline zeolite on the reaction product of zirconia appear to be similar to the effect observed of the zeolite upon a thoria catalyst. The principal effect observed is the reduction in methane formation. Some activity enhancement is evidence and aromatics distribution appears to be similar to that observed when using a ThO_2/ZSM-5 catalyst.

WHSV is the weight of feed/weight of catalyst X time in hours.

VHSV is the volume of gas/volume of catalyst X time in hours.

STP is identified as standard temperature of 0°C and 760 mm.Hg.

The effect of H_2S on ZrO_2/ZSM-5 catalyst activity was determined and reported in Table 1 below. The initial portion of the test (Run A) was run without H_2S to establish a base case. The operating conditions were 600 psig, 800°F and 1.3 WHSV (based on ZrO_2). After 20 hours on stream, about 3 wt.% of H_2S was introduced on a continuous basis with the H_2/CO syngas feed stream. A material balance was obtained after 26 hours continuous exposure to H_2S (Run B). Catalytic activity, unexpectedly and quite surprisingly, was unimpaired. A slightly higher conversion observed in Run B appears to be attributable to a lower WHSV for the run. The main influence attributable to H_2S appears to be to increase the methane yield (from 3.6% to about 11.2%) and to reduce aromatics formation. A significant amount of COS (carbonyl sulfide) was found in the effluent thus indicating that catalytic activity is also unaffected by this substance. The space velocity was then reduced to 0.26 WHSV (Run C). After an additional 24 hours on stream another material balance was made (Run C) which revealed a three-fold higher conversion and little change in selectivity. At the end of Run C, the H_2S was removed from the feed and after an additional 22 hours on stream, a product analysis was made. This analysis showed a drop in methane make and recovery of the catalyst selectivity for producing aromatics. See Run D. The analysis also showed a lower conversion which can be partially accounted for in the use of a somewhat higher (WHSV) space velocity during the period to obtain a material balance. Catalyst aging may also be a contributing factor. It is even possible to rationalize that the H_2S in the feed operates as a catalyst promoter. In any event the production of aromatics in Run D is higher than that obtained in Runs B and C.

TABLE 1

Effect of H_2S on ZrO_2/HZSM-5 Syngas Conversion Activity
$H_2/CO=1$, $H_2S \approx 3$ wt%

Run	A	B	C	D
	|← H_2S addition →|			
Reaction Conditions				
Temperature, °F	800	800	800	800
Pressure, psig	600	600	600	600
WHSV, hr^{-1} (a)	1.3	1.0	0.26	0.34
Time on Stream	20	46	70	92
Conversion, %				
CO	8.0	10.6	28.9	16.3
H_2	8.8	10.7	36.0	13.0
Total Effluent, wt%				
Hydrocarbons	2.7	3.7	13.1	6.8
H_2O	1.8	1.1	2.8	0.2
CO_2	3.6	8.2	14.1	9.1
CO	85.8	81.1	64.5	78.1
H_2	6.1	5.8	5.3	5.8
Other (b)	–	0.1	0.2	—
Hydrocarbons, wt%				
Methane	3.6	11.2	10.2	5.5
Ethane	7.9	8.5	11.7	12.4
Ethylene	0.2	0.2	—	—
Propane	12.6	19.6	13.6	12.1
Propylene	0.1	0.1	–	–
i-Butane	1.0	2.1	0.5	0.7
n-Butane	0.6	1.4	0.5	0.2
Butenes	—	—	—	—
C_5^+PON	–	0.2	0.1	–
Aromatics	74.0	56.7	63.4	69.1

(a) WHSV based on ZrO_2 component
(b) Mainly COS (H_2S-free basis)

Example 2.

Synthesis gas containing ~ 2.5% H_2S was converted to aromatic hydrocarbons over HfO_2/H2SM-5. The catalyst was found to be resistant to sulfur poisoning. This is demonstrated in the attached Table 6.

Sulfur (2.5%H_2S) was added to the syngas (synthesis gas) feed (LPA 130B). The results clearly demonstrate the ability of the catalyst to function in the presence of sulfur. As previously observed with ThO_2/HZSM-5 catalysts, the presence of sulfur tends to increase methane slightly with a subsequent decrease in aromatics.

A catalyst containing 35% TiO_2/65% HZSM-5 gives a conversion of syngas about 1/3 of that achieved with ZrO_2 and about ¼ of that achieved with HfO_2. Part of this lower conversion result is attributed to the lower TiO_2 content (35%). This TiO_2 data is shown in the attached table.

An experiment in which 0.5 wt.% of rare earth elements added to ZrO_2/HZSM-5 as a promoter is also shown in the attached table. The rare earth was added as the chloride salt.

TABLE 2

Syngas Conversion, Activity of Oxide Catalysts With HZSM-5

(H_2/CO=1)

Run No. LPA	130A	130B	128A (Comparative)	126A
Catalyst	50% HfO_2	50% HfO_2	35% TiO_2	50% ZrO_2/50%
	50% HZSM-5	50% HZSM-5	65% HZSM-5	HZSM-5+0.5% Rare Earth Mix
H_2S in feed (2.5 wt.%)	No	Yes	No	No
Reaction Conditions				
Temperature, °F	800	800	800	800
Pressure, psig	1200	1200	1200	1200
WHSV hr^{-1}	0.56	0.55	1.19	0.53
Time on Stream, hr.	73¾	98	21	21
Conversion, wt.%				
CO	7.7	12.3	3.3	13.0
H_2	7.6	12.2	3.8	11.2
Total Effluent, wt.%				
Hydrocarbons	3.1	4.0	1.3	4.5
H_2O	1.1	0.5	Tr	Tr
CO_2	3.4	7.8	2.0	8.4
CO	86.2	81.8	90.3	81.2
H_2	6.2	5.8	6.4	5.9
Other	—	0.1	—	—
Hydrocarbons, wt.%				
Methane	4.0	30.7	5.3	7.1
Ethane	14.3	15.6	36.2	31.6
Ethylene	—	0.1	—	0.1
Propane	8.2	16.6	20.4	20.5
Propylene	—	—	—	—
i-Butane	0.8	1.2	1.9	2.9
n-Butane	0.7	0.6	1.9	1.7
C_5+PON	0.3	0.3	0.7	0.5
Aromatics	71.7	34.9	33.6	35.6

WHAT WE CLAIM IS:—

1. A method for converting synthesis gas to hydrocarbon components in the gasoline range which comprises contacting synthesis gas at a temperature range of 400 to 1000°F with a carbon monoxide reducing catalyst comprising hafnium and/or zirconium, as metal, oxide and/or sulfide, in admixture with a crystalline aluminosilicate zeolite having a silica to alumina ratio of 12 to 3000 and a constraint index as herein defined within the range 1 to 12.

2. The method of Claim 1 wherein the hafnium and/or zirconium are employed in a sulfided form.

3. The method of Claim 1 wherein the carbon monoxide reducing catalyst initially comprises zirconium in the oxide form.

4. A method according to any preceding claim wherein the crystalline aluminosilicate is a zeolite of the ZSM-5 type as herein defined.

5. A method according to any preceding claim which is carried out at a temperature within the range of 500 to 850°F.

6. A method according to any preceding claim wherein gasoline boiling material comprising aromatics is formed at a pressure in excess of three atmospheres and at gas volume hourly space velocity in the range of from 500 to 50,000 volumes of gas.

7. A method according to any preceding claim wherein the admixture comprises a volume excess of crystalline aluminosilicate in relation to carbon monoxide reducing catalyst.

8. A method according to any preceding claim wherein the feed is sulphur-containing.

9. A method according to claim 1 of converting synthesis gas to hydrocarbons substantially as described in the foregoing Examples.

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