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(54) CONVERSION OF SYNTHESIS GAS TO HYDROCARBON MIXTURES

(71) We, MOBIL OIL CORPORATION, a Corporation 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:—

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

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

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

It has however not yet proved possible to identify any combination of catalyst and processing conditions which will yield liquid hydrocarbons in the gasoline boiling range which contain highly branched paraffins and substantial quantities of aromatic hydrocarbons, both of which are required for high quality gasoline; or to selectively produce aromatic hydrocarbons particularly rich in the benzene to xylenes range. A review of the status of this art is given in "Carbon Monoxide-Hydrogen Reactions", Encyclopedia of Chemical Technology, Edited by Kirk-Othmer, Second Edition, Volume 4, pp. 446—488, interscience Publishers, New York, N.Y.

Recently it has been discovered that synthesis gas may be converted to oxygenated organic compounds and these compounds then converted to higher hydrocarbons, particularly high octane gasoline, by catalytic contact of the synthesis gas with a carbon monoxide reduction catalyst followed by contacting the conversion products so produced with a special type of zeolite catalyst in a separate reaction zone. This two-stage conversion is described in DT—OS 2,438,252.

It has now been discovered that valuable hydrocarbon mixtures may be produced directly by reacting synthesis gas, i.e., mixtures of hydrogen and carbon monoxide, together possibly with other carbon oxides, or the equivalents of such mixtures, in the presence of certain heterogeneous catalysts comprising intimate mixtures of two or more components.

According to the invention, therefore, a process for producing hydrocarbons from synthesis gas comprises contacting such gas, at a temperature within the range of 400 to 1000°F, with a catalyst comprising a mixture of a metal or metal compound characterized by catalytic activity for the reduction of carbon monoxide and a crystalline aluminosilicate having a pore diameter greater than 5 Angstroms, a silica to alumina ratio of at least 12, and a constraint index as herein defined within the range of 1 to 12 and recovering gasoline boiling range hydrocarbons. The metal, or metal compound, comprises from 0.1 to 99, preferably from one weight percent to eighty weight percent, of the mixture. The carbon monoxide reduction component and the crystalline aluminosilicate may be in the same or separate particles.

The preferred crystalline aluminosilicates are ZSM—5, ZSM—11, ZSM—12, ZSM—35 and ZSM—38. The preferred metals are those of group VIII, but metals from groups IB (e.g. copper), IIB (e.g. zinc) and/or IIIB (e.g. thorium), and their compounds, may yield excellent results. Mixtures of all of these, together with promoters such as chromia, are of value.

The ratio of carbon monoxide reduction component to crystalline aluminosilicate may be adjusted to control product character, i.e. to determine whether gasoline boiling range components, paraffins/aromatics or internal olefins predominate.

The hydrogen to carbon oxides volume ratio is advantageously maintained within the range of from 0.2 to 6.0.

Depending on the choice of components and the particular reaction conditions employed, one may obtain substantial quantities of liquid mixtures which are rich in one or more olefins, branched paraffins, and aromatic hydrocarbons and are eminently suited for making high octane gasoline or petrochemicals. Thus, one may select catalyst and operating conditions to produce normally gaseous hydrocarbons having at least one carbon-to-carbon bond as the predominant product, or hydrocarbon streams rich in internal olefins. Such products have value as petrochemical feedstocks, and for the manufacture of liquefiable petroleum fuel. The catalysts employed not only produce highly desirable products with good selectivity but in many cases produce them either with extraordinarily high conversion per pass, or under mild conditions, or sometimes both. With thoria as the carbon monoxide reducing component, synthesis gas is converted at surprisingly low temperature and pressure. With a methanol synthesis catalyst of the zinc-copper-chromite-type as the reducing component, synthesis gas conversion rate is increased and large proportions of hydrocarbons having at least one carbon-to-carbon bond are obtained instead of methanol. With Fischer-Tropsch-type catalysts, increased quantities of aromatic hydrocarbons are obtained. Furthermore, when the preferred crystalline aluminosilicate component is used the catalytic activity is sustained for unusually long periods of time and aromatic hydrocarbons, when produced, are very rich in toluene and xylenes.

A typical purified synthesis gas will have the following volume composition, on a water-free basis: hydrogen, 51; carbon monoxide, 40; carbon dioxide, 4; methane, 1; and nitrogen, 4.

The synthesis gas may be prepared from fossil fuels by any of the known methods, including such in situ gasification processes as the underground partial combustion of coal and petroleum deposits. The term fossil fuels, as used herein, is intended to include anthracite and bituminous coal, lignite, crude petroleum, shale oil, oil from tar sands, natural gas, as sell as fuels derived from simple physical separations or more profound transformations of these materials, including coked coal, petroleum coke, gas oil, residua from petroleum distillation, and two or more of any of the foregoing materials in combination. Other carbonaceous fuels such as peat, wood and cellulosic waste materials also may be used.

The raw synthesis gas produced from fossil fuels will contain various impurities such as particulates, sulfur, and metal carbonyl compounds, and will be characterized by a hydrogen-to-carbon oxides ratio which will depend on the fossil fuel and the particular gasification technology utilized. In general, it is desirable for the efficiency of subsequent conversion steps to purify the raw synthesis gas by the removal of impurities. Techniques for such purification are known and are not part of this invention. However, it may not be necessary to remove substantially all the sulfur impurities when thoria is used as the carbon monoxide reducing component, since thoria is not irreversably poisoned by sulfur compounds. Furthermore, should it be required, it is preferred to adjust the hydrogen-to-carbon oxide volume ratio to be within the range of from 0.2 to 6.0 prior to use in this invention. Should the purified synthesis gas be excessively rich in carbon oxides, it may be brought within the preferred range by the well known water-gas shift reaction.

On the other hand, should the synthesis gas be excessively rich in hydrogen, it may be adjusted into the preferred range by the addition of carbon dioxide or carbon monoxide. Purified synthesis gas adjusted to contain a volume ratio of hydrogen-to-carbon oxides of from 0.2 to 6.0 will be referred to as "adjusted" synthesis gas.

Art-recognized equivalents of synthesis gas may also be employed. Mixtures of carbon monoxide and steam, for example, or of carbon dioxide and hydrogen, to provide adjusted synthesis gas by in situ reaction, are contemplated. Furthermore, when the process of the invention is used to produce hydrocarbon mixtures rich in aromatic hydrocarbons, as will be more fully described, a hydrogen-donor such as methane, methanol, or higher alcohols may advantageously be charged with the feed.

The component characterized by catalytic for the reduction of carbon monoxide may be selected from any of the art-recognized catalysts for producing hydrocarbons, oxygenated products, or mixtures thereof, from synthesis gas, and constitutes from 0.1 to 99, preferably from 1 to 80 percent by weight of the active components of the catalyst. Broadly, these components include those recognized as methanol synthesis catalysts, Fischer-Tropsh synthesis catalysts, and variants thereof. Commercial methanol synthesis catalysts comprising metals or oxides of zinc together with chromia, or of zinc and copper together with chromia or alumina, or known modifications of these, are included. In fact, synthesis gas will undergo conversion to form reduction products of carbon monoxide, such as alcohols and hydrocarbons, at from 300°F to 850°F, under from 1 to 1000 atmospheres pressure, over a fairly wide variety of catalysts. The prominent types of catalyst that induce conversion include the metals or oxides selected from the Groups consisting of IB, IIB, IIIB, IVB, VIB and VIII taken alone or in combination with one another. They particularly include the metals or oxides of zinc, iron, cobalt, nickel, ruthenium, thorium, rhodium and osmium. Fischer-Tropsch-type catalysts based on iron, cobalt, or nickel, and especially iron, are particularly suited for the production of oxygenated and hydrocarbon products that have at least one carbon-to-carbon bond in their structure. With the exception of ruthenium, all practical, art-recognized synthesis catalysts contain chemical and structural promoters. These promoters include copper, chromia, alumina, the alkaline earths, the rare earths, and alkali. Alkali, e.g., the carbonates of Group IA of the periodic table, and especially of potassium, is of particular importance with iron catalysts, since it greatly enhances the product distribution. Supports such as kieselguhr sometimes act beneficially.

It should be recognized that the carbon monoxide reducing component may be furnished as elemental metal or as corresponding metal compounds. Frequently in the preparation and use of such catalytic substances there will be one or more partial or complete transformations from elemental metal to compounds, or vice versa. By way of illustration, pure iron, roasted in an oxygen atmosphere in the presence of added aluminum and potassium nitrates provides a composition that contains 97% Fe_3O_4, 2.4% Al_2O_3, and 0.6% K_2O with trace amounts of sulfur and carbon. This composition after reduction with hydrogen at about 850°F catalyzes the conversion of synthesis gas at a temperature in the range of 360°F to 430°F, and at elevated pressures up to 20 atmospheres, 65% of the carbon monoxide being reduced to a mixture consisting of about one-third by weight of hydrocarbons boiling in the range to 200°F to 680°F, and about two-thirds of oxygenated compounds, mostly alcohols, in the same boiling range. Manganese nodules may be used as catalyst.

The crystalline aluminosilicate component of the heterogeneous catalyst is characterized by a pore dimension greater than 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, are characterized by a rigid crystalline framework structure composed of SiO_4 and AlO_4 tetrahedra cross-linked by the sharing of oxygen atoms; such a structure gives rise to precisely defined pores. Exchangeable cations are present to balance the negative charge on the AlO_4 tetrahedra.

The preferred zeolites useful in this invention are selected from a recently identified class of zeolites with unusual properties, by themselves being capable of catalyzing the transformation of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields. They are also generally highly effective in alkylation, isomerization, disproportionation and other reactions involving aromatic hydrocarbons. In many instances they have unusually low alumina contents, i.e. high silica to alumina ratios, and they are very active even with silica to alumina ratios exceeding 30. Furthermore they retain their crystallinity for long periods in spite of the presence of steam even at such high temperatures as induce irreversible collapse of the crystal framework of other zeolites, e.g. those of the X and A type. Carbonaceous deposits, when formed, may be removed from them by burning at higher than usual temperatures to restore activity, although in many environments they exhibit very low coke forming capability, conductive to very long times on stream between burning regenerations.

The silica to alumina ratios referred to pertains, of course, only to the tetrahedrally coordinated silicon and aluminum. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having ratios of at least 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water and can be termed "hydrophobic": such zeolites are advantageously employed in the present invention.

The zeolites useful as catalysts in this invention freely sorb normal hexane and have a pore dimension greater than 5 Angstroms. In addition, their structure must provide constrained accesss to some larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then entry of molecules of larger cross-section than normal hexane is substantially prevented 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:

Zeolite	C.I.
ZSM—5	8.3
ZSM—11	8.7
TMA Offretite	3.7
ZSM—12	2
Beta	0.6
ZSM—4	0.5
H—Zeolon	0.5
REY	0.4
Amorphous Silica-alumina	0.6
Erionite	38

It must, of course, be borne in mind that the very nature of this Index, and the technique by which it is determined, admit the possibility that a given zeolite can be tested under somewhat different conditions and thereby have different constraint indices. Constraint Index seems to vary somewhat with severity of operation (conversion). Therefore, it may be possible to select test conditions to establish multiple constraint indexes for a particular zeolite which may be both inside and outside the above defined range of 1 to 12. This invention includes within its scope any zeolite which manifests a constraint index in the range 1 to 12 at some combination of conditions within the scope of the determination procedure set forth above, whether or not it manifests an index outside that range at other such combinations of conditions.

This class of zeolites is particularly well exemplified by zeolites ZSM—5, ZSM—11, ZSM—12, ZSM—35 and ZSM—38. ZSM—5 is described in U.S. Specification 3,702,886; ZSM—11 in U.S. Specification 3,709,979; and ZSM—12 in U.S. Specification 3,832,449, ZSM—35 and 38 are two forms in which ZSM—21 can be synthesized and ZSM—21 is described in French patent specification 74 12078.

The specific zeolites described, when prepare 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 for from 15 minutes to 24 hours. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this special type zeolite, but does appear to favour it. Natural zeolites may sometimes be converted to this type of 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 ferricrite, brewsterite, stilbite, dachiardite, epistilbite, heulandite and chinoptilolite.

The zeolites may be used in the hydrogen form, metal-exchanged form or ammonium form. The metal cations that may be present include any of the cations of the metals of Groups I through VIII of the periodic table, although Group IA metal cations should not be present in large quantity.

The most preferred zeolites are those which have a crystal framework density, in the dry hydrogen form, of not substantially below 1.6 grams 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 in "Proceedings of the Conference on 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 of this invention 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 about 20 to about 150 microns, when intended for use in fluid bed operation; or they may be as large as up to about 1/2 inch for fixed bed operation. 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 associated with the crystalline aluminosilicate component by means such as impregnation of the zeolite with a salt solution of the desired metal, followed by drying and calcination. Base exchange of the 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 include precipitation of the carbon monoxide reduction component in the presence of the crystalline aluminosilicate; electroless deposition of metal on the zeolite; and 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, as will the necessity to avoid techniques likely to reduce the crystallinity of the crystalline aluminosilicate.

It will be clear from the foregoing that the mixtures used in the process of this invention may have varying degrees of intimacy. At one extreme, when using 1/2 inch pellets of the carbon monoxide reducing component mixed with 1/2 inch pellets of the crystalline aluminosilicate, substantially all locations within at least one of the components will be within not more than about 1/4 inch of some of the other component, regardless of the proportions in which the two components are used. With different sized pellets, e.g., 1/2 inch and 1/4 inch, again substantially all locations within at least one of the components will be within not more than about 1/4 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 crystalline aluminosilicate particles of about 0.1 micron particle size with colloidal iron 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 0.05 micron of some of the other component. This exemplifies about the highest degree of intimacy that is practical.

In the process of this invention, synthesis gas is contacted with the heterogeneous catalyst at a temperature of from 400°F to 1000°F, preferably from 500°F to 850°F, at a pressure from 1 to 1000 atmospheres, preferably from 3 to 200 atmospheres, and at a volume hourly space velocity from about 500 to 50,000 volumes of gas (STP) per volume of catalyst; or equivalent contact time if a fluidized bed is 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. 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.

Some embodiments of the invention are set forth by way of illustration in the following Examples.

Example 1.

Thoria was prepared according to the method of Pichler and Ziesecke, as described in "The Isosynthesis," U.S. Bureau of Mines Bulletin, 488 (1950), which involved essentially the precipitation of $Th(NO_3)_4$ solutions with Na_2CO_3 solutions followed by filtration, washing and drying at 100°C.

A composite catalyst was prepared by ball-milling equal weights of NH_4ZSM—5 and dried thoria gel, pelletizing and calcining at 1000°F for 10 hours. Three experiments were done, each one at 800°F, 1215 psia, and with a mixture of hydrogen and carbon monoxide having a H_2/CO ratio of 1.0. The first and second runs involved the thorium oxide and HZSM—5, each used separately, while the third run employed a heterogeneous catalyst containing both thorium oxide and HZSM—5.

The results are summarized in Table 1.

TABLE I.

Catalyst	(A) ThO$_2$ Alone	(B) HZSM—5 Alone	(C) ThO$_2$ plus HZSM—5
Contact Time - seconds (at reaction conditions)	15	15	15
Conversion, wt. %			
CO	5.3	<1	22.4
H_2	2.6	<1	15.2
Wt. % Hydrocarbons in total reaction effluent	0.6	0.2	5.5
Hydrocarbon Distribution (wt. %)			
Methane	41.0	39.6	17.3
C_2—C_4 hydrocarbons	58.6	60.4	73.8
C_5^+	0.4	—	8.9
	100.0	100.0	100.0
Aromatics in C_5^+, wt. %	Trace	Trace	41.6

Example 2.

A ZnO supported on Al_2O_3 was obtained from a commercial source and was used as the carbon monoxide reducing component. It contained 24% by weight of ZnO. HZSM –5 was used as the acidic crystalline aluminosilicate component.

The heterogeneous composite catalyst was prepared by ball-milling together four parts of the HZSM—5 to one part of the ZnO/Al_2O_3 catalyst, followed by pelletizing. Two runs were carried out, both at 600°F, 750 psia, and with a mixture of hydrogen and carbon monoxide having a H_2/CO ratio of 4. The first run used the ZnO/Al_2O_3 catalyst alone, while the second run employed a composite catalyst containing both the ZnO/Al_2O_3 and HZSM—5 catalysts.

The results are shown in Table 2.

TABLE 2.

Catalyst	(D) ZnO/Al$_2$O$_3$ Alone	(E) 20% ZnO/Al$_2$O$_3$ plus 80% HZSM—5 Composite
Contact Time — seconds (at reaction conditions)	25	25
Conversion, wt. %		
CO	32.0	6.7
H$_2$	5.4	3.4
Wt. % hydrocarbons in total reaction effluent	0.2	1.0
Hydrocarbon Distribution (wt. %)		
Methane	100.0	11.4
C$_2$—C$_4$ hydrocarbons	—	42.9
C$_5^+$	—	45.7
	100.0	100.0
Aromatics in C$_5^+$ (wt. %)	None	71.8

Example 3.

A methanol synthesis catalyst was prepared containing the following percentages by weight; copper — 54.55, zinc — 27.27, chromium — 9.09, and lanthanum — 9.09 on an oxygen-free basis. A composite catalyst was then prepared from equal parts of this component and HZSM—5, using 5% graphite as a binder. Two runs were made, each at 600°F, 750 psia, using as a feed a mixture of hydrogen and carbon monoxide with a H$_2$/CO ratio of 2 and are summarized in Table 3.

TABLE 3.

Catalyst	(F) Methanol Type Alone	(G) Methanol Type plus HZSM—5 Composite
Space Velocity on Methanol Catalyst Component (cc of synthesis gas/g. of methanol catalyst/hour)	5825	6764
CO Conversion wt. %	24	34
Wt. % in Water-Free Product		
Methane	0.7	1.1
C$_2$—C$_4$ Hydrocarbons	1.0	5.7
C$_5^+$ Hydrocarbons	1.0	1.8
	2.7	8.6

As shown, the contact times (reciprocal of space velocity) relative to the methanol catalyst component are very similar in the two runs; being slightly lower with the composite catalyst.

The composite catalyst shows a much greater production of hydrocarbons, particularly hydrocarbons higher in carbon number than methane, than the carbon monoxide reducing component by itself.

Example 4.

The carbon monoxide reducing component was a commercial iron oxide type ammonia synthesis catalyst containing small amounts of K, Ca and Al promoters. The zeolite component contained 65% HZSM—5 and 35% alumina binder. The heterogeneous composite catalyst contained 75% of the iron component and 25% of the zeolite component, and was made by ball-milling the components and then pelletizing the resultant powder.

Three runs were made at 700°F, 265 psia and with a mixture of hydrogen and carbon monoxide having a H_2/CO ratio of 1.0. Results are summarized in Table 4.

TABLE 4.

Catalyst	(H) Fe Component Alone	(J) Fe/HZSM—5 Components not mixed. Components in separate reaction zones in series	(K) Fe+HZSM—5 Composite catalyst, single reaction zone
Contact time — seconds (at reaction conditions)	15	30	15
Conversion, wt. %			
CO	93.5	96.9	98.4
H_2	67.8	76.9	72.3
Wt. % Hydrocarbons in total reaction effluent	22.6	25.6	25.5
Hydrocarbon Distribution (wt. %)			
Methane	44.6	50.1	52.6
C_2—C_4 hydrocarbons	50.1	41.1	41.4
C_5^+	5.3	8.8	6.0
Aromatics in C_5^+, wt. %	1.9	2.3	15.0

Experiment H illustrates the selectivity of the iron component in the absence of HZSM—5; the C_5^+ hydrocarbons contain only 1.9% aromatics. In experiment (J), a reaction zone containing HZSM—5 was placed after the reaction zone containing the iron catalyst. It can be seen that the aromatics selectivity was not significantly changed. In experiment (k), however, the intimate mixture of HZSM—5 with the iron component gave about a seven-fold increase in aromatics selectivity.

Example 5.

The catalyst in this example was prepared by impregnation of NH_4ZSM—5 containing 35% alumina binder with a solution of $Fe(NO_3)_3$, drying the catalyst and calcining at 1000°F for 10 hours. The finished catalyst contained 3% iron. Synthesis gas ($H_2/CO = 1$) was reacted over this catalyst at 700°F, 515 psia and 30 seconds contact time, giving the following conversions and products.

TABLE 5.

Catalyst	FeHZSM—5
Contact Time — seconds (at reaction conditions)	30
Conversion, wt. %	
CO	19.7
H_2	12.0
Wt. % Hydrocarbons in total reaction effluent	8.1
Hydrocarbon Distribution (wt. %)	
Methane	33.4
C_2—C_4 hydrocarbons	47.5
C_5^+	19.1
Aromatics in C_5^+, wt. %	24.6

Example 6.

The catalyst in this example was an intimate mixture of 57.4% ilmenite sand ($FeO \cdot TiO_2$), 21.3% HZSM—5 and 21.3% alumina binder. Synthesis gas ($H_2/CO = 1$) was reacted over said catalyst at 700°F, and 265 psia and 10 seconds contact time, giving the following conversion and products.

TABLE 6.

Catalyst	Ilmenite + HZSM—5
Contact Time — seconds (at reaction conditions)	10
Conversion, wt. %	
CO	62.3
H_2	48.3
Wt. % Hydrocarbons in total reaction effluent	21.5
Hydrocarbon Distribution (wt. %)	
Methane	29.2
C_2—C_4 hydrocarbons	59.1
C_5^+	11.7
Aromatics in C_5^+, wt. %	29.9

Example 7.

The catalyst in this example was an intimate mixture of 41.2% magnetite (Fe_3O_4), 29.4% HZSM—5 and 29.4% alumina binder. Synthesis gas ($H_2/CO = 1$) was reacted over said catalyst at 700°F, 265 psia and 10 seconds contact time, giving the following conversions and products.

TABLE 7.

Catalyst	Magnetite + HZSM—5
Contact Time — seconds (at reaction conditions)	10
Conversion, wt. %	
CO	41.8
H_2	37.6
Wt. % Hydrocarbons in total reaction effluent	16.6
Hydrocarbon Distribution (wt. %)	
Methane	31.0
C_2—C_4 hydrocarbons	55.0
C_5^+	14.0
Aromatics in C_5^+, wt. %	19.9

Example 8.

The catalyst in this example was an intimate mixture of 41.2% iron carbide, 29.4% HZSM—5 and 29.4% alumina binder. Synthesis gas ($H_2/CO = 1$) was reacted over said catalyst at 700°F, 265 psia and 10 seconds contact time, giving the following conversions and products.

TABLE 8.

Catalyst	Iron carbide + HZSM—5
Contact Time — seconds (at reaction conditions)	10
Conversions, wt. %	
CO	11.7
H_2	11.1
Wt. % Hydrocarbons in total reaction effluent	4.5
Hydrocarbon Distribution (wt. %)	
Methane	40.8
C_2—C_4 hydrocarbons	50.1
C_5^+	9.1
Aromatics in C_5^+, wt. %	6.2

Example 9.

The catalyst of this example was prepared by impregnating an extrudate comprising ZSM—5 crystalline zeolite containing about 35% alumina as binder with a solution of iron ($Fe(NO_3)_3$) followed by drying and reducing with hydrogen at a temperature of about 950°F. Three different levels of iron impregnation were prepared as identified in Table 10. Synthesis gas ($H_2/CO = 2$) was passed in contact with the catalyst at a temperature of 600°F. and a pressure of 200 psig. The results obtained are as follows:

TABLE 9.

EFFECT OF FE CONCENTRATION

"IMPREGNATED" ZSM—5 EXTRUDATE

600°F. BED SETTING, 200 PSIG, 2 H_2/CO, 3300 GHSV

Iron, Wt. %	8.6	14.8	21.7
CO Conversion, Wt. %	43	65	83
% Wt. C Converted to:			
CO_2	30	35	36
Hydrocarbon	70	65	64
Hydrocarbon Composition Wt. %.			
C_1	38	42	38
C_2	16	16	14
C_3	9	8	7
C_4	10	8	8
C_5	4	5	6
C_6^+	23	21	27
	100	100	100
C_6^+ Aromatics, Wt. %	46	42	34

Example 10.

The catalysts used in this example comprised a mixture of ZSM—5 alumina extrudate (65/35 ratio) with a copper methanol synthesis catalyst. In Runs 912—1 and 2, the volume ratio of ZSM—5/Cu synthesis catalyst was 2.9/2 and in Runs 913—3 to 5, the volume ratio of ZSM—5/Cu synthesis catalyst was 4/1. The ZSM—5 alumina extrudate was also mixed with an iron ammonia synthesis catalyst in a 4/1 ratio and used as the catalyst in Runs 903—1, and 6. The operating conditions employed and results obtained in the respective Runs are identified in Table 10 below.

TABLE 10.

Catalyst (14—25 Mesh)	HZSM—5		CuMethanol Synthesis Catalyst			HZSM—5		FeAmmonia Synthesis Catalyst
Vol. Ratio, HZSM—5/Syn. Cat.	2.9/2		4/1			4/1		
Pressure, psig.	200	400	750			200		
GHSV	2440	2600	1210			3420		3300
WHSV	1.56	1.66	0.86			1.62		1.56
Temp. °F. Bed Setting	600	650	600			600		
Average	604	659	614	612	608	615	618	615
Hot Spot	607	663	623	618	611	629	628	624
Run Time, Hours	19—1/2	20	20	24	20	24	24	21
Accum. ", Days	0.8	1.6	1.2	2.2	3.0	1	2	4.7
CO Conversion, wt. %	31	45	80	70	55	96	95	94
H_2 Conversion, wt. %	8	14	38	28	19	55	54	49
% Wt. C converted to: CO_2	49	45	45	46	46	32	32	35
Hydrocarbon	51	55	55	54	54	68	68	65

TABLE 10 (Continued).

Catalyst (14—25 Mesh)	HZSM—5		CuMethanol Synthesis Catalyst			HZSM—5	FeAmmonia Synthesis Catalyst	
Hydrocarbon composition, wt. %								
C_1	3	3	4	4	3	18	17	18
C_2	14	13	21	18	16	3	4	5
C_3	29	23	21	19	19	9	8	6
C_4	21	17	17	19	19	18	18	10
C_5	14	14	10	12	13	10	11	10
C_6^+	19	20	27	28	30	42	42	51
	100	100	100	100	100	100	100	100
Aromatics in C_6^+, wt. %	19	37	34	31	32	61	50	24
C_{10} aromatics in C_6^+, wt. %	9	24	32	29	28	<7	7	3
Tetra methyl benzenes	8	22	32	29	27	<1	>1	<1
Durene	3	12	17	16	15	1	<1	<1
Run No.	912—1	—2	913—3	—4	—5	903—1	—2	—6

Example 11.

A thoria-ZSM—5 catalyst (no alumina) prepared as identified in Example 1 above was used in two separate runs for comparison with a similar catalyst containing the alumina binder as shown below. In these examples synthesis gas ($H_2/CO = 1$) was passed in contact with the catalyst at a temperature of 800°F. and a pressure of 1200 psig. The results obtained are presented in Table 11 below.

TABLE 11.

SYNGAS CONVERSION OVER ThO_2/HZSM—5
800°F. 1200 PSIG, $H_2/CO = 1$

	ThO_2/HZSM—5 (No Al_2O_3)		ThO_2/HZSM—5 + Al_2O_3 binder
GHSV (STP), hr.$^{-1}$	205	205	375
Time on Stream, hr.	26	267	94
Conversion, wt. %			
CO	36.9	58.1	10.1
H_2	21.3	45.6	12.9
Total Product, wt. %			
Hydrocarbons	9.09	14.98	3.66
Oxygenates	—	—	—
H_2O	0.57	0.38	1.18
CO_2	25.69	29.99	4.10
CO	60.36	39.93	84.90
H_2	4.29	3.48	6.16
Hydrocarbons, wt. %			
Methane	13.6	11.3	9.7
Ethane	36.7	28.0	19.5
Ethylene	0.2	0.1	—
Propane	33.0	24.8	14.1
Propylene	0.2	0.2	—
i-Butane	5.4	4.3	1.7
n-Butane	3.8	2.7	0.9
Butenes	—	—	—
i-Pentane	1.8	0.9	0.6
n-Pentane	0.2	tr.	tr
Pentenes	—	—	—
C_6^+	0.4	—	tr
Aromatics	4.7	27.7	53.3
Total C_5^+	7.1	28.6	53.9
Aromatics in C_5^+	66.2	96.9	98.9

Example 12.

Ruthenium dioxide has been used as a Fischer-Tropsch catalyst to convert synthesis gas into paraffin wax under high pressure and low temperature (248-428°F). However, at higher temperature (572°F.), only methane is formed. Ruthenium-on-aluminum has also been used for synthesis conversion to produce gaseous, liquid and solid hydrocarbons; however, again, methane becomes the major product at temperatures higher than 482°F. No aromatics are produced using these catalysts. Now, it has been found that ruthenium, in combination with HZSM—5, produces aromatics-containing gasoline in high yield from synthesis gas over a wide temperature range.

Example A.

A 5% ruthenium on ZSM—5 catalyst was prepared by vacuum impregnating 10 g. of NH_4—ZSM—5 with a 18 ml. aqueous solution containing 1.25 g. $RuCl_3 \cdot 3H_2O$. After drying in vacuum the catalyst was air calcined in an oven at 1000°F. for two hours. This resulted in a conversion of the ammonium form of ZSM—5 to the hydrogen form.

Example B.

A 1% Ru/ZSM—5 catalyst was prepared using the procedure of Example A, except that 20 g. of NH_4—ZSM—5 with a 36 ml. aqueous solution containing 0.5 g. of $RuCl_3 \cdot 3H_2O$ was used.

Example C.

The conversion of synthesis gas (H_2/CO) was carried out in a fixed-bed continuous flow reactor. The stainless steel reactor was charged with 5.5 g. of the 5% Ru/ZSM—5 catalyst prepared in Example A; the catalyst was prereduced with flowing hydrogen at 750°F. and a pressure of 750 psig for three hours.

The conversion of synthesis gas (H_2/CO) was carried out at 750 psig. 580°F. WHSV = 0.32 and H_2/CO = 2/1. The results and the detailed hydrocarbon distribution are given in Table 13 below. High conversion with good selectivity to liquid (C_5^+) products was obtained. The liquid product contained 25% aromatics and had octane numbers R+O = 77 and R+3 = 92.

Example D.

Syngas conversion was carried out under essentially the same conditions as in Example C except that 5.5 g. of 1% Ru/ZSM—5 prepared in Example B was used. The results are listed in Table 12 below. High conversion to hydrcarbons rich in C_2+ and containing 13.8% aromatics was obtained.

TABLE 12.

Synthesis Gas Conversion over Ruthenium/HZSM—5 Catalyst at 750 psig. 580°F. WHSV = 0.32 and $H_2/CO = 2/1$

	Example C	Example D
Catalyst	5% Ru/HZSM—5	1% Ru/HZSM—5
Method of Catalyst Preparation	Impregnation	Impregnation
Conversion, wt. %		
CO	82.91	79.31
H_2	88.32	84.84
Total Reactor Effluent, wt. %		
Hydrocarbons	37.54	31.83
H_2	1.46	1.92
CO	14.95	18.07
CO_2	2.31	2.66
H_2O	43.74	45.53
Hydrocarbon Composition, wt. %		
C_1	31.11	20.42
C_2	6.61	4.02
C_3	6.82	7.79
C_4	9.22	16.78
C_5^+	46.24	50.99
Aromatics in C_5^+	24.84	27.04
Aromatics in C_6^+	29.57	34.78
Aromatics in Total H.C.	11.51	13.79
Hydrocarbon Selectivity*	98.50	97.60
Octane No. of C_5^+	77 (R+0)	
	92 (R+3)	

*(Total carbon converted — Total carbon in CO_2)/Total carbon converted.

WHAT WE CLAIM IS:—

1. A process for producing hydrocarbons which comprises contacting synthesis gas at a temperature within the range 400° to 1000°F and elevated pressure with a catalyst comprising a metal or metal compound having catalytic activity for the reduction of carbon monoxide and a crystalline aluminosilicate having a pore diameter greater than 5 Angstroms, a silica to alumina ratio of at least 12, and a constraint index as herein defined within the range of 1 to 12.

2. A process according to claim 1 wherein said metal or metal compound comprises from one to eighty weight percent of the catalyst.

3. A process according to claim 1 or claim 2 wherein said metal and said crystalline aluminosilicate are in the same particle.

4. A process according to any preceding claim wherein said metal is a Group VIII metal.

5. A process according to any of claims 1 to 3 wherein said metal is thorium.

6. A process according to any of claims 1 to 3 wherein said metal is copper and/or zinc.

7. A process according to any preceding claim wherein said crystalline aluminosilicate is zeolite ZSM—5, ZSM—11, ZSM—12, ZSM—35 or ZSM—38.

8. A process according to claim 7 wherein said zeolite is at least partly in the hydrogen form.

9. A process according to any preceding claim wherein the volume ratio of hydrogen to carbon oxides in the synthesis gas is within the range 0.2 to 6.0.

10. A process according to any preceding claim wherein the ratio of metal component to crystalline aluminosilicate is selected to promote the production of gasoline boiling range hydrocarbon.

11. A process according to any preceding claim wherein the catalyst composition and reaction conditions are selected to promote the production of paraffins and aromatic hydrocarbons.

12. A process according to any preceding claim wherein the catalyst composition and reaction conditions are selected to promote the production of internal olefins.

13. A process according to any of claims 1 to 12 wherein said metal or metal compound is present in the form of a Fischer-Tropsch catalyst.

14. A process according to any of claims 1 to 12 wherein said metal or metal compound is present in the form of a methanol synthesis catalyst.

15. A process according to claim 1 of producing hydrocarbons from synthesis gas substantially as described in any of the foregoing Examples.

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