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Schlinger et al.

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[54] CONVERSION OF HYDROGEN AND CARBON MONOXIDE INTO C₁-C₄ RANGE HYDROCARBONS

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[58] Field of Search 260/444.6 M, 449 M, 260/449.6 R, 449 R

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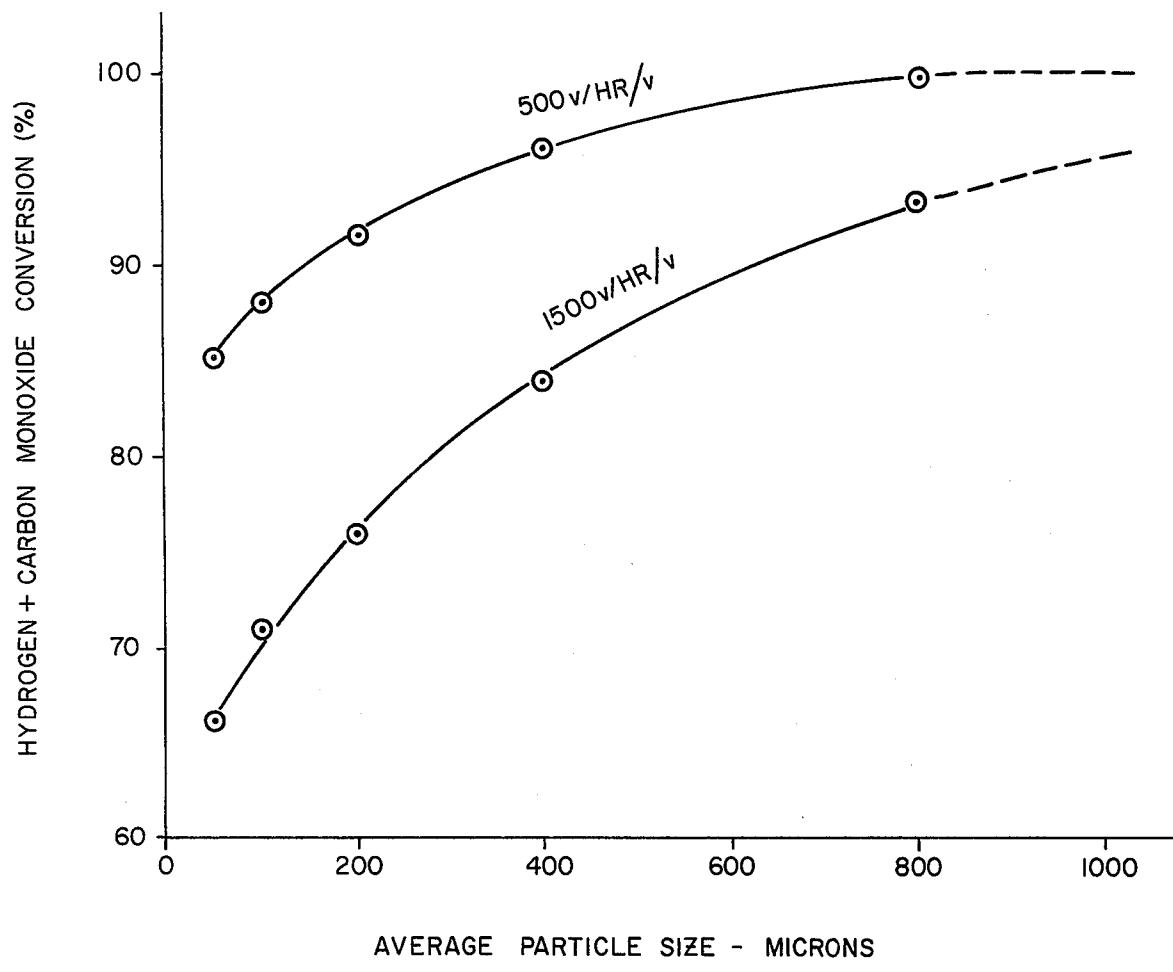
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[57] ABSTRACT

A process for conversion of hydrogen and carbon monoxide into hydrocarbons in the presence of an ebullient bed of catalyst comprising reduced iron oxide promoted with potassium equivalent to 2-10 pounds potassium carbonate per 1000 pounds iron oxide catalyst, and having an average particle size in the range of 100-1000 microns, wherein the catalyst is chlorided for increasing the yield of C₁-C₄ range hydrocarbons.

3 Claims, 1 Drawing Figure



CONVERSION OF HYDROGEN AND CARBON MONOXIDE INTO C₁-C₄ RANGE HYDROCARBONS

BACKGROUND OF THE INVENTION

The present invention relates to processes for converting hydrogen and carbon monoxide into hydrocarbon products. More particularly, the present invention relates to processes for conversion of hydrogen and carbon monoxide into C₁-C₄ range saturated hydrocarbons, particularly methane, in the presence of an iron based catalyst having improved activity and selectivity for production of C₁-C₄ range hydrocarbons from hydrogen and carbon monoxide.

Processes for production of gas streams comprising hydrogen and carbon monoxide from carbonaceous and/or hydrocarbon charge stocks are well known in the prior art. Of particular interest for providing hydrogen and carbon monoxide feed for the process of the present invention are processes for partial oxidation of hydrocarbons and/or carbonaceous charge stocks with molecular oxygen-containing gas. Such partial oxidation processes are widely practiced upon a commercial basis. In partial oxidation reactions, hydrocarbon or carbonaceous charge stocks, ranging from methane through coal or coke, are contacted with an amount of molecular oxygen insufficient for complete combustion of such charge stock, at temperatures in the range of about 1600° F. to about 3000° F. and pressures in the range of about 1-250 atmospheres, for conversion of the oxygen and charge stock into hydrogen and carbon monoxide. It is known to charge water or steam to partial oxidation reactions for increasing the ratio of hydrogen to carbon monoxide in the product gas. Also, it is known to maintain the reaction temperature within the range of about 1600°-2000° F. and to add water or steam to the partial oxidation reaction for production of a gas product comprising substantial amounts of methane as well as hydrogen and carbon monoxide. As no catalyst is employed in the partial oxidation reaction, it is not necessary to remove sulfur and other materials from the charge stock prior to the partial oxidation reaction. Sulfur is primarily converted to hydrogen sulfide (H₂S) and minor amounts of carbonyl sulfide (COS). In addition to hydrogen, carbon monoxide and methane, a minor portion of the hydrocarbon or carbonaceous charge stock is converted to carbon dioxide and about 0.5 to 5 weight percent is converted to soot. Processes for removal of impurities, such as hydrogen sulfide and carbon dioxide, from partial oxidation effluent gasses, and production of gasses substantially comprising hydrogen and carbon monoxide are well known in the prior art and are widely practiced.

The molar ratio of hydrogen to carbon monoxide in a product gas from partial oxidation processes may be increased substantially by subjecting such gas to the water gas shift reaction. The water gas shift reaction comprises heating the gas to a temperature of about 550° F. or higher and contacting said gas with steam in the presence of a suitable catalysts. Under such conditions carbon monoxide reacts with steam to form carbon dioxide and hydrogen. Carbon dioxide formed from the water gas shift reaction may be removed from the product gas by acid gas absorption techniques.

It is becoming increasingly desirable to convert low value hydrocarbon and carbonaceous fuels into more useful fuel products, particularly methane and low mo-

lecular weight C₁-C₄ range saturated hydrocarbons. Particularly, it is desirable to convert hydrocarbonaceous or carbonaceous charge stocks containing high percentages of impurities such as ash and sulfur into clean fuels which may be burned without contributing substantial pollution to the environment. Partial oxidation processes product gasses comprise hydrogen and carbon monoxide, which may be efficiently treated for removal of impurities which may lead to air pollution. However, the resulting gas products, substantially comprising hydrogen and carbon monoxide, have a relatively low heating value particularly when compared to naturally occurring fuel gasses such as methane. Therefore, conversion processes for reacting hydrogen with carbon monoxide for conversion into low molecular weight saturated hydrocarbons, particularly methane, have been developed. In such processes hydrogen and carbon monoxide in a molar ratio of from about 1:1 to about 4:1 and preferably in the range of about 1:1 to about 3:1 are contacted at pressures in the range of atmospheric to about 25 atmospheres and higher, and temperatures in the range of about 600° F. to about 900° F., in the presence of selected catalysts for conversion of hydrogen and carbon monoxide into low molecular weight saturated hydrocarbons. Catalysts which may be employed in such reactions include metals, preferably in subdivided form, such as iron, cobalt, nickel, vanadium, molybdenum, and tungsten, and compounds of these metals such as the halides, oxides, sulfides, molybdates, sulfates, or oxyates. Mixtures and other combinations of two or more of these metals and/or compounds of these metals may be employed as desired. Exemplary of such prior art processes for conversion of hydrogen and carbon monoxide is the process disclosed in U.S. Pat. No. 3,730,694, D. K. Wunderlich, issued May, 1973. In such processes, the heat of reaction from the conversion of hydrogen and carbon monoxide is substantial and means for removing such heat of reaction must be provided to prevent a rapid increase in temperature which, if uncontrolled, would damage the catalyst and/or damage the processing equipment. Methods for controlling the temperature in such conversion reactions, include recycling inert gasses, such as a portion of the product gas, and providing indirect heat exchange such as steam coils, within the catalyst bed. One known method for removing the heat of reaction and thereby controlling the conversion reaction temperature is to employ catalyst in finely subdivided form (less than 100 microns) and fluidizing said catalyst with gas charged to the process to form a dense phase fluidized bed. Heat exchange means, such as steam generation coils, are suspended within said fluidized bed for absorption of the heat of reaction. Such fluidized beds have very good heat transfer properties which allow rapid, even transfer of heat from the catalyst bed to the heat removal means, e.g., the steam coils.

The more reactive catalysts for conversion of hydrogen and carbon monoxide, particularly those containing nickel, are poisoned by sulfur and sulfur compounds. Such poisoning results in the catalysts losing activity for conversion of hydrogen and carbon monoxide. Whereas, catalysts which are more tolerant of sulfur, particularly iron containing catalysts, have lower initial activity for conversion of hydrogen and carbon monoxide. Therefore, in processes of the prior art, hydrogen and carbon monoxide charged to such conversion reactions are commonly treated for substantially complete

removal of sulfur and sulfur compounds if a highly active nickel-based catalyst is to be employed. Otherwise, use of more sulfur tolerant catalysts results in lower conversion of hydrogen and carbon monoxide into the desirable low molecular weight hydrocarbon compounds.

SUMMARY OF THE INVENTION

Now, according to the present invention, an improved process employing improved iron-containing catalysts is disclosed for converting hydrogen and carbon monoxide into low molecular weight saturated hydrocarbons. The improved catalysts have increased activity over iron-containing catalysts of the prior art, and have physical properties which allow efficient transfer of the heat of reaction from the catalysts to heat exchange means such as steam generation coils.

The process of the present invention comprises contacting hydrogen and carbon monoxide, in a molar ratio in the range of at least 1:1 to about 3:1 respectively, at a reaction temperature in the range of about 600° to 1000° F., a pressure in the range of about 200 to 3000 psig, and a space velocity in the range of about 250 to 2,500 standard volumes carbon monoxide plus hydrogen per hour per volume of catalyst (v/hr/v), in the presence of an ebullient bed of an improved iron-based catalyst.

In one embodiment of the present invention, the improved catalyst consists essentially of iron oxide selected from mill scale and/or magnetite ground to an average particle size in the range of about 100 to about 1000 microns (preferably 350-800 microns); wherein said ground iron oxide is treated with a water soluble potassium compound, such as potassium carbonate, in an amount sufficient to provide potassium in an amount equivalent to about 2 to 10 pounds of potassium carbonate per 1000 pounds of iron oxide; wherein said potassium containing iron oxide is chemically reduced with hydrogen; and wherein said reduced catalyst is treated with chlorine, or a compound suitable for chloriding the catalyst (e.g. HCl, methylchloride, etc). The catalyst is treated, at process operating conditions set-out above, periodically with chlorine gas or a compound suitable for chloriding the catalyst in an amount sufficient for increasing the yield of C₁-C₄ range saturated hydrocarbons at the expense of unsaturated hydrocarbons, higher molecular weight hydrocarbons, and organic chemicals such as alcohols and organic acids.

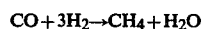
Advantages of the present invention include a process for conversion of hydrogen and carbon monoxide into a low molecular weight saturated hydrocarbons in the C₁-C₄ range employing a sulfur-tolerant, iron-based catalyst having good heat transfer properties and having improved activity over iron-based catalysts of the prior art. These and other advantages will be discussed in the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a graphical representation showing hydrogen and carbon monoxide conversion as a function of catalyst particle size for unchlorided catalysts at conditions of constant hydrogen-carbon monoxide molar ratio, temperature, pressure, and space velocity. Hydrogen and carbon monoxide conversion is shown at space velocities of 500 and 1500 v/hr/v.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, feed gas to the conversion reaction is a gas containing substantial amounts of hydrogen and carbon monoxide in molar ratio of at least 1:1 to about 3:1 respectively. Generally, since the product of this conversion reaction is C₁-C₄ range saturated hydrocarbons, the feed gas is selected from products of such reactions as partial oxidation of relatively high molecular weight hydrocarbons and/or carbonaceous materials. The feed gas may contain other materials, such as carbon dioxide, as well as other hydrocarbons such as methane, ethane, propane and butanes. Preferably, a major portion of the feed gas will be made up of hydrogen, carbon monoxide, and C₁ to C₄ range hydrocarbons, both saturated and unsaturated. Hydrogen is preferably present in the feed gas in a molar amount sufficient to react with all the carbon monoxide and unsaturated hydrocarbons present such that the hydrocarbon components of the reaction product will essentially comprise C₁-C₄ range hydrocarbons which are useful as clean burning fuel. The hydrogen to carbon monoxide molar ratio should be above 1:1 to prevent excess coke formation, but does not need be as high as 3:1, as might be inferred from the following equation:



The iron based catalyst of the present invention is a good carbon monoxide shift catalyst. So, if the system is deficient in hydrogen, some of the carbon monoxide will react with water present (either from the feed gas or produced in the reaction) to form additional hydrogen. Such additional hydrogen is available for reaction with carbon monoxide.

The reaction temperature favors formation of hydrogen, the hydrogen to carbon monoxide molar ratio in effluent gas from the conversion reaction is appreciably greater than in the feed. Since the hydrogen to carbon monoxide molar ratio in the effluent gas from the conversion reaction is greater than in the feed, effluent gas may be recycled for increasing the hydrogen to carbon monoxide molar ratio in the conversion reaction. Preferably, at least a portion of the water and carbon dioxide reaction by products are removed from the effluent gas prior to recycle. Water may be condensed from the effluent gas, and carbon dioxide may be removed by acid-gas absorption techniques, for example absorption into monoethanolamine or into diethanolamine.

Impurities in the feed gas, such as hydrogen sulfide and carbonyl sulfide, may be conveniently removed by conventional absorption techniques such as absorption into monoethanolamine, diethanolamine, etc. Complete removal of such impurities is not required, and if they comprise only a small proportion of the feed gas, removal may be unnecessary.

Iron-based catalyst of the present invention is prepared iron oxide selected from magnetite and/or mill scale ground and screened to a selected average particle size distribution in the range of about 100 to 1000 microns, preferably in the range of 350-800 microns. Such particle size distribution is critical in preparing the improved catalysts of the present invention, as catalysts of smaller particle size distribution show substantially reduced activity for conversion of hydrogen and carbon monoxide. Catalysts having particle size distributions larger than about 1000 microns do not have substan-

tially greater activity and are difficult to maintain in a fluidized or ebullient condition, which difficulty leads to problems in transferring the large amounts of exothermic heat of the conversion reaction from the catalyst bed to heat exchange means such as steam generation coils.

The ground and screened magnetite and/or mill scale is impregnated with a water solution of a potassium compound, such as potassium carbonate, in an amount sufficient to provide potassium in an amount equivalent to about 2 to about 10 pounds, and preferably about 7 pounds of potassium carbonate per 1000 pounds of iron oxide. Upon drying, the potassium-impregnated magnetite and/or mill scale is chemically reduced by contacting with molecular hydrogen at an elevated temperature and pressure. Hydrogen, flowing at a superficial gas velocity of about 0.1 to about 2 ft/sec., having a pressure of about 100–1000 psig, is contacted with the potassium-impregnated iron oxide at a temperature in the range of about 650°–800° F. for a time sufficient to reduce chemically a substantial portion of the magnetite and/or mill scale.

Upon impregnation with potassium and reduction with hydrogen, the catalyst is useful in a Fischer-Tropsch reaction for conversion of hydrogen and carbon monoxide into olefins, higher molecular weight hydrocarbons, alcohols and organic acids, without further treatment or conditioning step. In such a Fischer-Tropsch reaction, however, the yield of saturated C₁–C₄ range hydrocarbons is quite low.

According to the present invention, we have discovered that treating the potassium-containing, reduced iron catalyst with chlorine or a compound suitable for chloriding the catalyst results in a catalyst having substantially improved selectivity for production of C₁–C₄ range hydrocarbons from conversion of hydrogen and carbon monoxide. Employing such catalyst in the critical size range of 100–1000 microns as discussed above, results in improved conversion rates for hydrogen and carbon monoxide compared to iron catalysts of the prior art.

In the present invention, the potassium-containing reduced iron catalyst may be chlorided prior to use in a hydrogen and carbon monoxide conversion process, or may be chlorided during such conversion process.

For chloriding, the potassium-containing reduced iron catalyst is contacted with chlorine gas at an elevated temperature in the range of about 200° F. to about 900° F. in an amount and for a time sufficient to chloride at least the surface of said catalyst. Preferably, the chlorine gas employed for chloriding the catalyst is diluted with an inert gas, such as nitrogen. For example, 14.1 cubic feet of potassium containing reduced iron catalyst was treated with 105 SCF of a gas consisting of 2 volume percent chlorine in nitrogen, over a period of 12 minutes at 413 psig and 653° F. This treatment which amounted to about one SCF chlorine gas per seven cubic feet of catalyst was sufficient to activate the catalyst for production of good yields of C₁–C₄ range hydrocarbons from conversion of hydrogen and carbon monoxide.

The improved chlorided catalyst of the present invention, in the size range disclosed herein, is useful in reactions for converting hydrogen and carbon monoxide into high yields of C₁–C₄ range saturated hydrocarbons. Such conversion reactions are operated at temperatures in the range of about 600°–900° F. preferably 650°–800° F., and pressures in the range of about

200–3000 psig, preferably 400–1500 psig. Formation of saturated hydrocarbons is favored by higher pressures, such that use of higher pressures, consistent with structural limitations of process equipment, is desirable. In the conversion reaction a fresh feed gas stream comprising hydrogen and carbon monoxide, having a hydrogen to carbon monoxide molar ratio of at least 1:1 to about 3:1, is contacted with the catalyst of the present invention at operating conditions including space velocities of about 250 to 2,500 SCF hydrogen plus carbon monoxide per hour per cubic foot of catalyst (v/hr/v), (preferably about 500 to 1500 v/hr/v). Effluent gas from the conversion reaction is richer in hydrogen compared to carbon monoxide. That is, the effluent gas has a higher H₂:CO ratio than the feed gas. Preferably, a portion of this effluent gas is recycled to the conversion reaction for increasing the molar ratio of hydrogen to carbon monoxide in the reaction zone, and for improving overall conversion of hydrogen and carbon monoxide. Recycle ratios of about 0.5:1 to about 2:1 or higher, volumes recycle gas per volume of feed gas may be employed in the conversion reaction. The conversion reaction effluent gas contains substantial amounts of carbon dioxide and water as well as hydrocarbons, and unconverted hydrogen and carbon monoxide. It is preferred to treat the effluent gas for removal of liquid hydrocarbons, carbon dioxide and water prior to recycle to the conversion reaction.

The hydrogen and carbon monoxide conversion reaction contemplated herein is exothermic. Large amounts of the heat of hydrogen and carbon monoxide reaction must be removed from the reaction zone. Within contemplation of the present invention, the improved catalyst, having average particle sizes in the 100–1000 micron range, is maintained in a vertical reactor vessel to provide an ebullient catalyst bed height in the range of 5 to 30 feet, preferably 10 to 25 feet. The feed and recycle gases are charged to the bottom of the reactor vessel at a rate sufficient to provide a superficial vapor velocity in the range of about 1 to 10 feet per second, such that the bed of catalyst is expanded and maintained in an ebullient condition by the upward flowing gases. Such ebullition provides excellent heat transfer throughout the catalyst bed, preventing hot spots and aiding transfer of the heat of reaction from all parts of the bed to the heat exchange means. For ebullient beds such as these wherein large heats of reaction must be removed, heat exchange means comprising steam generation tubes or coils are very useful. Vertical tubes for generating steam are particularly useful for removing heat from the present reaction. Within the operating ranges of the conversion reaction disclosed herein, it has been found that vertical steam generating tubes in number sufficient to provide from about 2.5 to about 3.5 square feet of tube surface per cubic foot of ebullient catalyst are sufficient to remove the heat of reaction from the catalyst bed.

EXAMPLE I

To demonstrate the effect of particle size upon catalyst conversion activity and selectivity, a series of runs were performed employing catalysts of various average particle sizes for conversion of hydrogen and carbon monoxide into useful products.

The catalysts were prepared by grinding magnetite ore in a hammer mill, in separate grinding steps, to produce samples of ground ore having average particle sizes respectively of 50, 100, 200, 400 and 800 microns.

Each sample of ground ore was subjected to magnetic separation for removal of extraneous mineral matter present in the ore. Each sample of separated magnetite was treated with an aqueous solution of K_2CO_3 in an amount sufficient to provide about 7 pounds of K_2CO_3 per 1000 pounds of magnetite, and the treated magnetite was chemically reduced by contact with hydrogen, at a temperature of about 650° F., a pressure of about 200 psig, a hydrogen superficial gas velocity of about 0.8 ft/sec, for a period of about 12–15 hours, until evolution of water ceased.

The reduced catalyst samples were then employed in processes for conversion of hydrogen and carbon monoxide into higher molecular weight products. In each of the conversion processes, a sample of catalyst of selected average particle size was loaded into an ebullient bed reactor in an amount sufficient to provide an ebullient catalyst bed height of about 23 ft. The exothermic heat of the hydrogen and carbon monoxide conversion

reactions are removed from the reactor ebullient bed by indirect head exchange with water contained in vertical pipes suspended within the reactor. The reactor ebullient bed temperature was controlled by controlling the pressure (and consequently the temperature) of steam generated within the vertical pipes suspended in the reactor.

A series of reaction runs were performed with each catalyst sample, wherein the space velocity of hydrogen and carbon monoxide was varied in the range of 500–1500 volumes hydrogen plus carbon monoxide per hour per volume of catalyst, while reaction temperature, pressure, and gas recycle ratio were maintained constant. In each run, for each catalyst sample, reaction temperature was about 660° F., reaction pressure was about 414 psig, and recycle volume ratio was about one volume recycle gas per volume fresh hydrogen plus carbon monoxide feed gas. The molar ratio of hydrogen to carbon monoxide in the fresh feed gas was 2:1.

In each run, fresh hydrogen plus carbon monoxide, in a molar ratio of about 2:1 respectively was combined with recycle gas (described below) and was flowed into the bottom of the reactor vessel at a temperature of about 200° F. Within the reactor vessel, the up flowing gases contacted the catalyst bed under conditions for conversion of hydrogen and carbon monoxide at superficial vapor velocities such that the catalyst was expanded into an ebullient bed (and for smaller particle size catalyst the bed was fluidized). The exothermic heat of hydrogen and carbon monoxide conversion was transferred by indirect heat exchange into the vertical tubes wherein steam was generated at a controlled pressure for maintaining the temperature of the ebullient catalyst bed at about 660° F. The temperature throughout the ebullient bed was substantially constant and hot spots were avoided. Effluent gas comprising conversion products and unreacted hydrogen and carbon monoxide was continuously removed, free of entrained catalyst, from the top of the reactor vessel and was cooled in a condenser to condense normally liquid hydrocarbon, organic chemicals, and water. The cooled reactor effluent was separated into a gas phase comprising light hydrocarbons, carbon dioxide and unreacted hydrogen and carbon monoxide and a liquid phase comprising normally liquid hydrocarbons, organic chemicals, and wa-

ter. A portion of the gas phase equal in volume to the fresh hydrogen and carbon monoxide feed was returned to the reactor as recycle gas. The remaining portion of the gas phase, comprising carbon dioxide, light hydrocarbons and unreacted hydrogen and carbon monoxide was analyzed to determine the overall conversion of hydrogen and carbon monoxide within the reactor.

Batches of catalyst, having average particle sizes of 50, 100, 200, 400 and 800 microns, were employed in hydrogen and carbon monoxide conversion reactions as described above, at space velocities of 500 and 1500 SCF hydrogen plus carbon monoxide per hour per cubic foot of catalyst. Molar conversion of hydrogen and carbon monoxide was determined for each catalyst sample at each space velocity. Results of these experimental conversion reactions are shown in the drawing attached to this specification.

In the drawing, the conversion of hydrogen and carbon monoxide is expressed as percent conversion, e.g.

$$\% \text{Conv.} = \frac{\text{fresh (H}_2\text{O} + \text{CO}) + \text{recycle (H}_2\text{O}) - \text{effluent (H}_2 + \text{CO})}{\text{fresh (H}_2 + \text{CO}) + \text{recycle (H}_2 + \text{CO})} \times 100$$

Percent conversion is plotted versus catalyst particle size for reaction space velocities of 500 v/hr/v and 1500 v/hr/v. As can be seen in the drawing, the percentage conversion of hydrogen and carbon monoxide increased as the average particle size increased, within the range of about 50 to 800 microns. A projection of the catalyst activity curves in the drawing indicates that catalyst activity does not increase further with an increase in particle size above about 1000 microns. This result is surprising and unexpected, for it is commonly believed that catalyst activity increases with increased catalyst surface area, and that surface area increases with decreasing particle size. This is the first indication that catalyst having large average particle size is more active than the same catalyst having a smaller average particle size.

EXAMPLE 2

The following experiment was performed for conversion of hydrogen and carbon monoxide to demonstrate the effectiveness of treating the reduced iron catalysts disclosed herein with chlorine for increasing the yield of C_1 – C_4 range hydrocarbons at the expense of heavier hydrocarbons and organic chemicals.

A magnetite ore was ground in a hammer mill to produce a sample having 350 micron average particle size. The ground magnetite was subjected to magnetic separation for removal of extraneous mineral matter present in the ore. The separated magnetite was treated with an aqueous solution of potassium carbonate in an amount sufficient to provide about 7 pounds of potassium carbonate per 1000 pounds of magnetite, and the treated magnetite was dried.

The potassium carbonate treated magnetite was loaded into an ebullient bed reactor, containing steam generation tubes for heat removal, wherein the magnetite was chemically reduced by contact with hydrogen at a temperature of about 650° F., a hydrogen velocity of about 0.8 ft/sec, for a period of about 12–15 hours until evolution of water ceased.

After reduction, the resulting catalyst was employed in a hydrogen and carbon monoxide conversion reaction to obtain product yields for comparison with yields obtained with the chlorided catalyst which is described

below. Operating conditions and results of this comparison run with the unchlorided catalyst are shown as Run 1 in Table I, below.

Upon completion of Run 1, the hydrogen plus carbon monoxide feed to the reactor was continued, at operating conditions of temperature and pressure, and the catalyst was chlorided by flowing 105 SCF of a gas comprising 2 volume percent chlorine diluted with nitrogen into the bottom (inlet) of the reactor over a period of 12 minutes. The reactor contained 14.1 cubic feet of catalyst, consequently the chloriding treatment amounted to about one SCF chlorine gas per seven cubic feet of catalyst. Upon completion of this treatment, Run 2 was commenced for converting hydrogen and carbon monoxide in the presence of the chlorine treated catalyst. Operating conditions and results of this reaction with chlorided catalyst are shown as Run 2 in Table I, below.

Upon completion of 48 hours of operation in Run 2, a second 100 SCF of gas comprising 2 volume percent chlorine diluted with nitrogen was injected into the reactor within a period of about 12 minutes. Upon addition of this chlorine containing gas, the hydrogen and carbon monoxide conversion reaction was continued an additional 48 hours whereupon a third 100 SCF of gas comprising 2 volume percent chlorine in nitrogen was injected into the reactor over a period of about 12 minutes. Upon addition of this third volume of chlorine containing gas, the hydrogen and carbon monoxide conversion reaction was continued. Operating conditions and results of the hydrogen and carbon monoxide conversion reaction, after injection of the third volume of chlorine containing gas, are shown as Run 3 in Table I, below.

In the hydrogen and carbon monoxide conversion reactions of this Example, the catalyst in the reactor vessel was expanded by upflowing charge gas to form an ebullient bed of about 23 ft. height. The exothermic heat of the conversion reaction was removed from the ebullient bed by indirect heat exchange with steam generated within steam tubes suspended within the reactor vessel.

In Runs 1, 2 and 3, hydrogen plus carbon monoxide space velocity, reaction temperature, reaction pressure and gas recycle ratio were maintained about constant. Recycle gas was obtained by cooling the effluent gas from the reaction zone in a condenser to condense normally liquid hydrocarbons, organic chemicals and water. The cooled reactor effluent was separated into a gas phase comprising light hydrocarbons, carbon dioxide and unreacted hydrogen and carbon monoxide and a liquid phase comprising normally liquid hydrocarbons, organic chemicals and water. A portion of the gas phase equal in volume to the fresh hydrogen and carbon monoxide feed gas was returned to the reactor as recycle gas. Composition analyses of fresh hydrogen and carbon and monoxide feed, recycle gas, product gas and product liquid were performed to determine product yields for Runs 1, 2 and 3 respectively.

From examination of the operating conditions and results of Runs 1, 2 and 3 shown in Table I, it can be seen that using the chlorided catalyst of the present invention in a hydrogen and carbon monoxide conversion reaction (Run 2) results in product yield containing substantially more C₁-C₄ range hydrocarbon than the product yield from a conversion reaction (Run 1) employing unchlorided catalyst. Additionally, the yield of C₁-C₄ range hydrocarbons was further increased upon

additional treatment of the catalyst with chlorine (Run 3). Further, the amounts of heavier hydrocarbons and organic chemicals (e.g. alcohols and acids) were substantially reduced when chlorided catalyst was employed. Consequently, the amount of gaseous C₁-C₄ range hydrocarbons useful as fuel gas was substantially increased when the chlorided catalyst of the present invention was employed.

TABLE I

RUN NUMBER	1	2	3
Catalyst: Particle Size, Microns	350	350	350
Catalyst Age: Hours	241	261	353
H ₂ + CO, Combined feed			
Mol. % H ₂	48.5	48.5	48.5
CO	21.9	21.9	21.9
Inlet pressure, psig	413	414	412
Temperature, °F.	653	661	661
Recycle Ratio	0.97:1	0.94:1	0.89:1
H ₂ + CO Space Velocity (v/hr/v)	891	878	992
Conversion:			
%CO	94.51	93.89	89.93
%H ₂	79.54	81.17	78.38
%H ₂ + CO	85.05	85.95	82.92
Yield C ₁ +			
lb. prod./MCF H ₂ + CO charge	11.023	10.704	9.081
lb. prod./MCF H ₂ + CO converted	12.961	12.454	11.02
Product distribution, wt. % of C ₁ +			
CH ₄	11.21	19.36	31.16
C ₂ H ₄	5.39	2.19	2.02
C ₂ H ₆	4.63	13.86	15.95
C ₃ H ₆	11.20	9.91	7.39
C ₃ H ₈	1.58	5.55	8.98
C ₄ H ₈	8.01	8.91	7.82
C ₄ H ₁₀	1.99	3.03	3.48
C ₅ Hydrocarbons	41.71	32.10	19.52
Alcohols	10.86	4.29	3.33
Acids	3.43	0.80	0.35
C ₁ -C ₄ Hydrocarbons	44.01	62.81	76.8

It is to be understood that modifications and variations of the process disclosed in the foregoing specification will occur to those skilled in the art, which modifications and variations are within the spirit and scope of the present invention. Consequently, the only limitations of the present invention intended are those included in the appended claims.

We claim:

1. In a process for conversion of hydrogen and carbon monoxide into C₁-C₄ range hydrocarbons; which comprises:

Forming an ebullient bed of particulate conversion catalyst in a reaction zone, with a feed gas comprising hydrogen and carbon monoxide in a molar ratio in the range of at least 1:1 to about 3:1 respectively, at a reaction temperature in the range of about 600° to about 1000° F., a reaction pressure in the range of about 200 to about 3000 psig, a hydrogen plus carbon monoxide space velocity in the range of about 25 to about 2500 v/hr/v, and a superficial vapor velocity in the range of about 1 to about 10 ft/sec, wherein said conversion catalyst is a chlorided, reduced iron catalyst promoted with potassium in an amount equivalent to from about 2 to about 10 pounds potassium carbonate per 1000 pounds of iron oxide; the improvement comprising maintaining in said reaction zone said catalyst having an average particle size in the range of about

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350 to about 800 microns, for conversion of said hydrogen and carbon monoxide into C₁-C₄ range saturated hydrocarbons.

2. The process of claim 1, wherein said conversion catalyst comprises iron oxide selected from the group consisting of mill scale, magnetite, and mixtures thereof, ground to a particle size in the range of about 350 to about 800 microns, treated with an aqueous solution of potassium carbonate in an amount sufficient to deposit upon said ground iron oxide about 2-10 pounds potassium carbonate per 1000 pounds iron oxide, chemically

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reduced with hydrogen, and subsequently chlorided at a temperature in the range of about 200° F. to 900° F. in an amount of at least about one SCF chlorine gas per seven cubic feet of catalyst, for increasing the yield of C₁-C₄ range hydrocarbons.

3. The process of claim 2 wherein said reduced iron catalyst is periodically treated with additional chlorine for maintaining the selectivity of said catalyst for conversion of hydrogen and carbon monoxide into C₁-C₄ range hydrocarbons.

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