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(54) CATALYST AND PROCESS FOR CONVERSION OF HYDROCARBONS

(71) We, ATLANTIC RICHFIELD COMPANY, a corporation organised and existing under the laws of the State of Pennsylvania, United States of America, of Arco Plaza, 515 Flower Street, Los Angeles, California, 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 relates to the conversion of hydrocarbons and more particularly to the chemical conversion of hydrocarbons promoted by catalyst which is periodically regenerated to remove carbonaceous deposits.

The terms "hydrocarbon conversion" and "hydrocarbon chemical conversion" as used herein, in general, refer to those chemical reactions for improving the octane number of gasoline or converting heavy hydrocarbons to light, low boiling hydrocarbons, or converting one or more hydrocarbons to one or more different hydrocarbon products. Hence, among those reactions included in such terms are isomerization, cracking, polymerization, alkylation, dealkylation, disproportionation and the like. Each of these "hydrocarbon conversions" is preferably carried out in the substantial absence of added free molecular hydrogen.

Each such "hydrocarbon conversion" is often carried out commercially by contacting a hydrocarbon feedstock with a solid catalytic material at conditions at which the desired hydrocarbon chemical conversion takes place. However, such conditions also allow formation of carbonaceous material, such as coke, which deposits on the catalyst. These deposits are periodically removed as they tend to inactivate the catalyst. The catalyst may be regenerated by burning or combusting at least a portion of such carbonaceous deposit material from the catalyst in the presence of free oxygen. During the catalyst regeneration carbon

monoxide and carbon dioxide are often produced as gaseous combustion products, the relative amounts of each depending upon the efficiency of the oxidation step.

Recent federal and local air pollution control legislation has made it necessary to eliminate or drastically reduce the amount of carbon monoxide being discharged into the atmosphere. The amount of carbon monoxide as a gaseous by-product from hydrocarbon conversion processes using a regenerative catalyst can be reduced by using a catalyst which contains a promoter, usually a metal or metal compound, for the conversion of carbon monoxide to carbon dioxide.

Such carbon monoxide oxidation catalyst systems employing metal oxidation promoters have met with varying degrees of success. One problem which has become apparent is the tendency of such oxidation catalysts to rapidly deactivate. This tendency is especially apparent when the oxidation catalyst comprises a Group VIII, platinum group metal component. Thus, carbon monoxide oxidation catalysts which are satisfactory, e.g. reduce carbon monoxide emissions to meet or approach governmental standards, in the virgin state, have been found to lose a substantial amount of carbon monoxide oxidation activity after a relatively short time in hydrocarbon conversion-catalyst regeneration service.

This invention provides an improved process for hydrocarbon conversion and an improved hydrocarbon conversion catalyst.

In accordance with the invention, there is provided a process for converting a hydrocarbon feedstock which comprises (1) contacting said feedstock in at least one reaction zone with a catalyst comprising solid particles substantially free of added platinum group metal components and capable of promoting the conversion of said feedstock at hydrocarbon conversion conditions to produce at least one hydrocarbon product and to cause deactivating carbonaceous material to be formed on said solid

particles, thereby forming deposit-containing particles; and (2) contacting said deposit-containing particles in at least one regeneration zone with an oxygen-containing
5 vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of said solid particles
10 and to form at least one carbonaceous deposit material combustion product; and (3) repeating steps (1) and (2) periodically, and in which there are circulated between said reaction zone and said regeneration
15 zone in intimate admixture with said solid particles, a minor amount of discrete entities comprising (A) a major amount by weight of alumina and (B) a minor, catalytically effective amount of at least one platinum
20 group metal component disposed on said alumina, said metal component being capable of promoting the oxidation of carbon monoxide to carbon dioxide at the conditions of step (2), thereby promoting
25 the oxidation of carbon monoxide to carbon dioxide in said regeneration zone.

Typical of reactor-regenerator arrangements having circulating catalyst bed systems are the conventional moving bed
30 reactor-regenerator system and the fluidized catalyst bed reactor-regenerator system. Both of these circulating bed systems are conventionally used in hydrocarbon conversion, e.g. hydrocarbon cracking, operations.

35 The platinum group metals are platinum, palladium, osmium, iridium, ruthenium and rhodium. The preferred platinum group metals are palladium and platinum, most preferably platinum. The preferred relative
40 amounts of the solid particles and discrete entities are 80 to 99 parts and 1 to 20 parts by weight, respectively. This catalyst system is especially effective for the catalytic cracking of a hydrocarbon feedstock to
45 lighter, lower boiling products. The present catalyst system has improver properties. For example, this catalyst system has improved carbon monoxide oxidation catalytic activity stability.

50 The catalyst system used in the process of the present invention is comprised of a mixture of two types of solid particles. The form, i.e. particle size, of the present catalyst, e.g. both solid particles and
55 discrete entities, is not critical provided it is such that the catalyst can be circulated between the reaction zone and the regeneration zone, and may vary depending, for example, on the type of reaction-regeneration
60 system employed. Such catalyst particles may be formed into any desired shape such as pills, cakes, extrudates, powders, granules and spheres using conventional methods. For example, spherical particles
65 having a diameter of 0.03 inch to 0.25 inch,

preferably 0.03 inch to 0.15 inch, are often useful in moving catalyst bed operations. With regard to fluidized catalyst bed systems, it is preferred that the major
70 amount by weight of the present catalyst particles have a diameter in the range of 10 microns to 250 microns, more preferably 20 microns to 150 microns.

The first solid particles are capable of promoting the desired hydrocarbon conversion
75 and are substantially free of added platinum group metal components.

The second solid particles, i.e., discrete entities, comprise (A) a major amount, i.e.,
80 at least 50% by weight, of alumina and (B) a minor amount of at least one platinum group metal component disposed on the support and capable of promoting the conversion of carbon monoxide to carbon
85 dioxide at carbon monoxide oxidizing conditions, e.g., conditions existing during contacting the deposit-containing first solid particles with an oxygen-containing gaseous medium to combust at least a portion of
90 the carbonaceous deposit material from the first solid particles.

The composition of the solid particles useful in the present invention is not critical, provided that such particles are
95 capable of promoting the desired hydrocarbon conversion. Particles having widely varying compositions are conventionally used as catalysts in such hydrocarbon conversion processes, the particular composition
100 chosen being dependent, for example, on the type of hydrocarbon chemical conversion desired. Thus, the solid particles suitable for use in the present invention include at least one of the natural or synthetic
105 materials which are capable of promoting the desired hydrocarbon chemical conversion. For example, when the desired hydrocarbon conversion involves one or more of hydrocarbon cracking, disproportionation, isomerization, polymerization, alkylation
110 and dealkylation, such suitable materials include acid-treated natural clays such as montmorillonite, kaolin and bentonite clays; natural or synthetic amorphous materials, such as amorphous silica-alumina,
115 silica-magnesia and silica-zirconia composites; and crystalline aluminosilicates, often referred to as zeolites or molecular sieves. In certain instances, e.g., hydrocarbon cracking and disproportionation, the solid
120 particles preferably include such crystalline aluminosilicates to increase catalytic activity. Methods for preparing such solid particles are conventional and well known in the art. For example, crystalline aluminosilicate
125 compositions can be made from alkali metal silicates and alkali metal aluminates so that they initially contain significant concentrations of sodium. Sodium tends to reduce the catalytic activity of the compo-
130

sition for hydrocarbon conversion reactions such as hydrocarbon cracking and disproportionation. Accordingly, most or all of the sodium in the crystalline aluminosilicate is removed or replaced, e.g., with other metal cations such as calcium or aluminium ions or ions of the rare earths. This can be accomplished by ion exchanging the crystalline aluminosilicate with soluble compounds of calcium, aluminium or the rare earths. It may also be desirable to substitute at least some of the sodium ions with hydrogen ions. This can be accomplished by contacting the crystalline aluminosilicate with a source of hydrogen ions such as acids, or hydrogen precursors such as ammonium compounds. These procedures are thoroughly described in U.S. Patent 3,140,253 and United States Reissue Patent 27,639.

Compositions of the solid particles which are particularly useful in the present invention are those in which the crystalline aluminosilicate is incorporated in an amount effective to promote the desired hydrocarbon conversion, e.g., a catalytically effective amount, into a porous matrix which comprises, for example, amorphous material which may or may not be itself capable of promoting such hydrocarbon conversion. Included among such matrix material are clays and amorphous compositions of silican-alumina, magnesia, zirconia and mixtures of these. The crystalline aluminosilicate is preferably incorporated into the matrix material in amounts within the range of 1% to 75%, more preferably 2% to 50%, by weight of the total solid particles. The preparation of crystalline aluminosilicate-amorphous matrix catalytic materials is described in the above-mentioned patents.

As indicated above, the discrete entities utilized in the present invention comprise a major amount of alumina and a minor amount of at least one platinum group metal component disposed on the support and present in an amount sufficient to promote the oxidation of carbon monoxide to carbon dioxide. It is preferred that the discrete entities comprise a major amount of alumina having a surface area of from 25 m.²/g. to 600 m.²/g. or more. The alumina comprises a major amount, preferably at least 70%, and more preferably at least 90%, by weight of the discrete entities. Suitable aluminas for use in the discrete entities are those aluminas derived from hydrous alumina predominating in alumina trihydrate, alumina monohydrate, amorphous hydrous alumina and mixtures thereof. Alumina in the form of chi-, gamma-, delta-, eta-, kappa-, and theta-alumina is preferred, while gamma- and eta-alumina are more preferred. Minor,

substantially non-interfering proportions of other well known refractory materials, e.g., inorganic oxides such as silica, zirconia, magnesia and the like may be included in the present discrete entities. By "substantially non-interfering" is meant amounts of other materials which do not have a substantial deleterious effect on the present catalyst system or hydrocarbon conversion process. In another preferred embodiment, the present discrete entities further comprise a minor amount of at least one aluminosilicate capable of promoting the desired hydrocarbon conversion. Typical aluminosilicates have been described above. Preferably, such aluminosilicates comprise 1% to 20%, more preferably 1% to 10%, by weight of the discrete entities. The presence of such aluminosilicates in the present discrete entities acts to increase the overall catalytic activity of the solid particles-discrete entities mixture for promoting the desired hydrocarbon conversion.

The alumina may be synthetically prepared in any suitable manner and may be processed prior to use by one or more treatments including drying, calcination and steaming. Thus, for instance, hydrated alumina in the form of a hydrogel can be precipitated from an aqueous solution of a soluble aluminium salt such as aluminium chloride. Ammonium hydroxide is a useful agent for effecting the precipitation. Control of the pH to maintain it within the values of 7 to 10 during the precipitation is desirable for obtaining a good rate of conversion. Extraneous ions, such as halide ions, which are introduced in preparing the hydrogel, can, if desired, be removed by filtering the alumina hydrogel from its mother liquor and washing the filter cake with water. Also, if desired, the hydrogel can be aged, say for a period of several days. The effect of such aging is to build up the concentration of alumina trihydrate in the hydrogel. Such trihydrate formation can also be enhanced by seeding an aqueous slurry of the hydrogel with alumina trihydrate crystallites, for example, gibbsite.

The alumina-based composition may be formed into particles of any desired shape such as pills, cakes, extrudates, powders, granules and spheres using conventional methods. The size selected for the particles can be dependent upon the intended environment in which the final discrete entities is to be used. In a further preferred embodiment, the support of the discrete entities has substantially the same chemical composition as the catalyst useful in promoting the desired hydrocarbon conversion, e.g., the present solid particles, as described above. Thus, the support of the discrete entities can provide additional

hydrocarbon conversion catalytic activity.

As indicated above, the discrete entities utilized in the present invention also contain at least one platinum group metal component disposed on the support. The metal, such as platinum, may exist within the final discrete entities at least in part as a compound such as an oxide, sulfide or halide, or in the elemental state. Generally, the amount of the metal component present in the final discrete entities is small compared to the quantity of the support. In general, it is desirable to incorporate into the discrete entities 0.05 parts per million (ppm.) to 10% and preferably 0.5 ppm. to 1%, by weight of the metal, based on the total weight of the discrete entities. The platinum group metal component preferably comprises from 0.05 ppm. to 1%, more preferably 0.05 ppm. to 1,000 ppm., and still more preferably 0.5 ppm. to 500 ppm., by weight of the discrete entities, calculated on an elemental basis. Excellent results are obtained when the discrete entities contain 50 ppm. to 200 ppm., by weight of at least one platinum group metal component.

The metal component may be incorporated in the discrete entities in any suitable manner, such as by co-precipitation or co-gellation with the support, ion-exchange with the support, or by the impregnation of the support at any stage in its preparation and either after or before calcination of the support. Preferably, the metal component is substantially uniformly disposed on the support of the present discrete entities. One preferred method for adding the metal to the support involves the utilization of a water soluble compound of the metal to impregnate the support. For example, platinum may be added to an alumina support by co-mingling the uncalcined alumina with an aqueous solution of chloroplatinic acid. Other water-soluble compounds of platinum may be employed as impregnation solutions, including, for example, ammonium chloroplatinate and platinum chloride.

Both inorganic and organic compounds of the metals are useful for incorporating the metal component into the present discrete entities. Typical inorganic compounds for incorporation into the second solid particles include ruthenium nitrate, ruthenium chloride, rhodium trichloride, ammonium palladium hexachloride, palladium chloride, diamminedichloropalladium, diamminedinitropalladium, tetraamminepalladium chloride, tetraamminepalladium hydroxide, palladium nitrate, palladium acetate, osmium tetroxide, ammonium platinum hexachloride, chloroplatinic acid, diamminodichloroplatinum, diamminedinitroplatinum and tetraammineplatinous

hydroxide.

Typical organic compounds include ruthenocene, tricarbonyltris(triphenylphosphino)ruthenium, palladium acetylacetonate, tetrakis(triphenylphosphino)palladium, dichloro(ethylene) palladium (II) dimer, π -cyclopentadienyldicarbonylosmium(I)dimer, platinum acetylacetonate, dichlorocarbonylplatinum platinum (II), trimethylplatinum chloride dichlorotetracarbonyldirhodium (I), chlorocarbonylbis(triphenylphosphino) rhodium (I), triiodotricarbonyliridium (III) and trichlorobis(trichlorophosphino) indium (III).

It may be desirable to be able to separate the discrete entities from the solid particles, for example, when it is desired to use the solid particles alone for hydrocarbon conversion or where it is desired to recover the discrete entities for other uses or for platinum group metal recovery. This can be conveniently accomplished by preparing the second solid particles in a manner such that they have a different size than the first solid particles. The separation of the first and second solid particles can then be easily effected by screening or other means of size segregation.

Preferably, the discrete entities have improved attrition resistance relative to the solid particles. Such improved attrition resistance may be obtained in any suitable manner. For example, the fully composited discrete entities can be contacted in a reducing, inert or oxidizing atmosphere at elevated temperatures, preferably in the range of 1200°F. to 3000°F. and more preferably 1600°F. to 2500°F., for a time sufficient to increase the attrition resistance of the discrete entities. Such time is preferably in the range of 1/2 hour to 48 hours or more, more preferably 1 hour to 16 hours. In a preferred embodiment, the alumina support of the discrete entities is contacted at elevated temperatures to improve attrition resistance. After such contacting, the catalytically active platinum group metal components are incorporated into the support using suitable techniques described above. Such discrete entities have been found to exhibit increased attrition resistance and to be effective to promote the oxidation of carbon monoxide.

An additional means for improving the attrition resistance of the discrete entities, particularly such entities which are larger than 500 microns in diameter and include an amount of silica in the support, involves the use of glazing components. Thus, the fully composited discrete entities are contacted with a minor amount, preferably 0.01% to 2% by weight of the total discrete entities, of at least one material selected from the group consisting of compounds of alkali metals, alkaline earth metals and boron at temperatures above

1000°F. sufficiently high as to induce "fusion" between the added composition and adjacent portions of the discrete entity surface.

5 The following compounds are representative of those which can be used either singly, or in any desired combination, to form the glazing composition for application to the discrete entities: NaCl, Na₂CO₃,
 10 KCl, K₂CO₃, LiF, Li₂SO₄, Cs₂CO₃, Rb₂CO₃, Na₄SiO₄, Na₂Si₂O₇, Na₂SiO₃, CaSiO₂, BeF₂, BeCl₂, BeO, BeCO₃, MgO, MgCl₂, MgSO₄, MgCO₃, CaO, Ca₃(PO₄)₂, CaF₂, CaCO₃, Ca oleate, Ca naphthenate, Mg oxalate, Ca
 15 sulfonate, Na oleate, SrO, SrCO₃, SrF₂, BaCl₂, BaCO₃, BaO, Banaphthenate, B₂O₃, H₃BO₄, Na₂B₄O₇·10H₂O, Ca₂(BO₃)₂, CaB₄O₇ and Mg₃(BO₃)₂. Particularly good results have been obtained with CaCO₃, B₂O₃,
 20 Na₂B₄O₇ (including hydrates), H₃BO₃, BaCO₃ and compositions containing 1-25% MgO, 30-75% CaCO₃ and 25-50% Ca₃(PO₄)₂, by weight. In this preferred grouping, it is intended that carbonates may be replaced in whole or in part by the
 25 equivalent oxides, since the latter are formed at glazing temperatures, in any event. In glazing discrete entities for employment in petroleum hydrocarbon cracking operations, it is preferred not to utilize halides or alkali
 30 metal salts in the glazing composition. For further details of such glazing procedures, see U.S. Patents 3,030,300 and 3,030,314. When glazing discrete entities which do
 35 not contain silica, the glazing composition preferably comprises at least one metal salt, e.g., silicate, capable of decomposing to form silica at the elevated temperatures noted above.
 40 In certain instances, e.g., where the solid particle have been equilibrated at severe hydrocarbon conversion conditions and/or over a lengthy period of time, a minor amount of the solid particles may have
 45 attrition resistance equal to or greater than the discrete entities. However, in the preferred embodiment of the present invention employing discrete entities which have improved attrition resistance, the reference
 50 to improved attrition resistance is relative to the co-mingled solid particles taken as a whole, or, in other words, relative to the average of the solid particles. Preferably, the discrete entities are at least 10% and
 55 more preferably, at least 20% more attrition resistant than the average of the solid particles with which they are co-mingled. The attrition resistant discrete entities of the present invention have a longer average
 60 service life in conventional hydrocarbon conversion reactor-regenerator systems than the co-mingled solid particles. The present discrete entities reduce losses of valuable carbon monoxide oxidation promoters while
 65 providing effective carbon monoxide oxida-

tion and not unduly detrimentally affecting the desired hydrocarbon conversion.

Although this invention is useful in many hydrocarbon chemical conversions, the present process finds particular applicability
 70 in systems for the catalytic cracking of hydrocarbons and the regeneration of catalysts so employed. Such catalytic hydrocarbon cracking often involves converting, i.e., cracking, heavier or higher
 75 boiling hydrocarbons to gasoline and other lower boiling components, such as hexane, hexene, pentane, pentene, butane, butylene, propane, propylene, ethane, ethylene, methane and mixtures thereof. Often, the
 80 substantially hydrocarbon feedstock comprises a gas oil fraction, e.g., derived from petroleum, shale oil, tar sand oil or coal. Such feedstock may comprise a mixture of straight run, e.g., virgin, gas oil. Such gas
 85 oil fractions often boil primarily in the range of 400°F. to 1000°F. Other substantially hydrocarbon feedstocks, e.g., other high boiling or heavy fractions of petroleum, shale oil, tar sand oil and coal,
 90 may be cracked using the apparatus and method of the present invention. Such substantially hydrocarbon feedstocks often contain minor amounts of contaminants, e.g., sulfur and nitrogen.
 95

Hydrocarbon cracking conditions are well known and often include temperatures in the range of 850°F. to 1100°F., preferably 900°F. to 1050°F. Other reaction conditions usually include pressures of up to 100 psig.;
 100 catalyst to oil ratios of 1 to 5 to 25 to 1; and weight hourly space velocities (WHSV) of from 3 to 60. These hydrocarbon cracking conditions are not critical to the present invention and may be varied
 105 depending, for example, on the feedstock and solid particles being used and the product or products wanted.

In the process of the invention, the catalyst is cycled between the reaction zone
 110 where the hydrocarbon conversion takes place and a regeneration zone for restoring the catalytic activity of the solid particles of catalyst previously used to promote the hydrocarbon cracking. Carbonaceous
 115 deposit-containing catalyst particles from the reaction zone are contacted with free oxygen-containing gas in the regeneration zone at conditions to restore or maintain the activity of the catalyst by removing, i.e.,
 120 combusting, at least a portion of the carbonaceous material from the catalyst particles. The conditions at which such contacting takes place are not critical to the present invention. The temperature in
 125 the catalyst regeneration zone of a hydrocarbon cracking system is often in the range of 900°F. to 1500°F., preferably 900°F. to 1300°F. and more preferably 1100°F. to 1300°F. Other conditions within
 130

such regeneration zone include, for example, pressures up to 100 psig., average catalyst contact times within the range of 3 minutes to 120 minutes, preferably from 5 3 minutes to 75 minutes. Sufficient oxygen is preferably present in the regeneration zone to completely combust the carbonaceous deposit material, for example, to carbon dioxide and water. The amount of 10 carbonaceous material deposited on the catalyst in the reaction zone is preferably in the range of 0.005% to 15%, more preferably 0.1% to 10%, by weight of the catalyst. At last a portion of the regenerated catalyst 15 is often returned to the hydrocarbon cracking reaction zone.

The solid particles useful in the catalytic hydrocarbon cracking embodiment of the present invention may be any conventional 20 catalyst capable of promoting hydrocarbon cracking at the conditions present in the reaction zone, i.e., hydrocarbon cracking conditions. Similarly, the catalytic activity of such solid particles is restored at the 25 conditions present in the regeneration zone. Typical among these conventional catalysts are those which comprise amorphous silica-alumina and at least one crystalline aluminosilicate having pore diameters of 8Å 30 to 15Å and mixtures thereof. When the solid particles and/or discrete entities to be used in the hydrocarbon cracking embodiment of the present invention contain crystalline aluminosilicate, the compositions 35 may also include minor amounts of conventional metal promoters such as the rare earth metals, in particular, cerium.

The catalyst, i.e., mixture comprising solid particles and discrete entities, and 40 process of the invention can be beneficially used for the disproportionation of paraffinic or aromatic hydrocarbons. For example, the present invention is well adaptable to the disproportionation of paraffinic hydrocarbons containing 3 to 20 carbon atoms 45 per molecule and aromatic hydrocarbons containing one or two rings and from 7 to 18 carbon atoms per molecule. The process of the invention is particularly useful for the disproportionation of methylbenzenes containing 7 to 10 carbon atoms 50 per molecule and is especially useful for the disproportionation of toluene to mixed xylenes and benzene. When disproportionating specific hydrocarbons it is often desirable to add a higher molecular weight hydrocarbon to the feedstock for the purpose of increasing the yield of a desired 55 product. For example, when disproportionating toluene to benzene and mixed xylenes the yield of xylenes can be increased by introducing higher methylbenzenes with the toluene feed. These higher methylbenzenes usually have 9 to 10 carbon atoms 65 and 1 to 4 methyl groups, and thus other

alkyl groups such as ethyl or propyl groups may be present. Thus, the aromatic streams available as a source of methyl groups for alkylation of toluene frequently do not consist only of methylaromatics. For 70 example, the C₉+ product obtained from a xylene isomerization process normally contains substantial ethyl (and possibly higher alkyl) ring substituents. Ethyl or higher 75 alkylaromatic substituents tend to crack more readily than methyl groups to form olefins and the parent aromatic ring. Higher temperatures also promote the cracking reaction. As a result, the preferred 80 conditions for a particular operation can be dependent on the composition of the C₉+ stream, the extent to which the C₉+ stream is recycled, and the ratio of benzene to xylenes desired in the product. In a process 85 involving recycle, the ethyl substituents may also be controlled by fractionating and removing a portion of the stream rich in n-propylbenzenes and ethyltoluenes, or rich in ethylxylenes. The C₉+ hydrocarbons can be obtained from various sources such as 90 naphtha reformat and coal tar, and in addition, the concentration of aromatics in the hydrocarbon streams can be increased by fractionation or solvent extraction procedures. Thus, trimethylbenzenes, for ex- 95 ample, those formed as by-products of the disproportionation reaction, can be incorporated in the toluene feed, thus effecting additional xylene production through transalkylation. The amount of the higher 100 methylaromatics added to the feed, either from an external supply or by recycling, can be a small amount effective to increase the xylene/benzene ratio in the product, as 105 5 to 60, preferably 15 to 50, weight percent based on the toluene fed to the reaction zone.

In accordance with a preferred embodiment a hydrocarbon feedstock, such as toluene, which is in the vapor phase is 110 disproportionated in a moving catalyst bed reactor in which the catalyst comprises a mixture of 80 to 99% by weight of solid particles which contain 5% to 50% of a crystalline aluminosilicate having a pore 115 size of at least 5Å disposed in a porous matrix of silica-alumina and 1% to 20% of discrete entities comprising 1% to 20% by weight of a crystalline aluminosilicate of substantially the same pore size as the 120 crystalline aluminosilicate included in the solid particles, at least 80% by weight of alumina and 0.05 ppm. to 1000 ppm. by weight of at least one platinum group metal component disposed substantially 125 uniformly in the alumina. The disproportionation reaction zone is preferably operated at a temperature of 700°F. to 1200°F. and more preferably 800°F. to 1000°F. and preferably at approximately 130

atmospheric pressures such as 0 psig. to 30 psig. The catalyst holding time, i.e., the average length of time that the catalyst remains in the reaction zone is preferably 5 kept in the range of 6 to 240 and more preferably 12 to 120 minutes.

After the catalyst particles leave the disproportionation reaction zone they enter the catalyst regeneration zone where at least a portion of the carbonaceous substances which were deposited on the catalyst particle surfaces during the disproportionation reaction are removed. This is accomplished by contacting the catalyst with an oxygen-containing gas stream, such as air, at temperatures preferably in the range of 800°F. to 1500°F. and more preferably 900°F. to 1200°F. The temperature and flow rate of the oxygen-containing gas stream is preferably such that the temperature in the regeneration zone is maintained in the preferred temperature range specified above.

The following examples clearly illustrate the present invention. However, these examples are not to be interpreted as specific limitations on the invention.

EXAMPLE I

This example illustrates certain of the advantages of the present invention.

A quantity of alumina-based particles of substantially pure gamma alumina, which is derived from a mixture of alumina monohydrate and amorphous hydrous alumina, in the shape of spheres having a diameter of 1/16 - 1/4 inch is charged into a vessel equipped with means for evacuating the vessel. These spheres can be obtained, for example, by the conventional oil-drop method. The vessel is evacuated and maintained under a vacuum of about 28 inches Hg for 20 minutes. An aqueous solution of chloroplatinic acid is introduced into the vessel and the vessel is agitated sufficiently to effect a substantially uniform distribution of the platinum on the alumina particles. The concentration of chloroplatinic acid in the solution is sufficient to impregnate the alumina with about 100 ppm., based on weight, of platinum, calculated as elemental platinum. The resulting discrete entities are dried in a hot air stream for three hours and then calcined in an air stream at 1200°F. for one hour.

EXAMPLE II

Example I is repeated except that substantially all of the alumina based particles have diameters in the range of 50 microns to 100 microns. Such particles can be obtained by conventional spray drying techniques. As in Example I, the final discrete entities contain about 100 ppm. of platinum, by weight of the total discrete entities, calculated as elemental platinum. Also, as in Example I, the platinum is substantially

uniformly distributed in the discrete entities.

EXAMPLE III

A quantity of solid particles of a commercially available hydrocarbon conversion catalyst containing about 6% by weight of crystalline aluminosilicate, about 54% by weight amorphous silica-alumina and 40% by weight alpha alumina, and having the same approximate size as the discrete entities from Example I, is combined with the discrete entities of Example I so that a mixture of 5 parts by weight of discrete entities and 95 parts by weight of the solid particles results. The catalytic activity of the solid particles is equalibrated by using same (prior to combining with the discrete entities) in commercial moving-bed hydrocarbon conversion service.

The mixture of solid particles and discrete entities is loaded to a conventional TCC moving catalyst bed reaction-catalyst regeneration system. Briefly, this system causes catalyst particles to flow by gravity from a supply hopper through a reaction zone, where the catalyst is contacted with hydrocarbon feedstock at hydrocarbon conversion conditions and the desired hydrocarbon chemical conversion takes place. The catalyst then flows to a catalyst regeneration zone where the catalyst is contacted with an oxygen-containing gaseous medium to combust at least a portion of the catalyst carbonaceous deposits which are formed in the reaction zone. The regenerated catalyst leaves the regeneration zone and is air lifted back to the supply hopper and the cycle is repeated.

Toluene is disproportionated in this moving catalyst bed reactor system loaded with the catalyst mixture. The catalyst is advanced through at a rate such that each particle has an average residence time in the reaction zone of about 50 minutes. With equilibrium conditions achieved the reaction zone temperature is maintained at about 955°F. and a reaction zone pressure of between 5 psig. and 20 psig. is maintained. Toluene is fed into the reactor at a weight hourly space velocity (WHSV) of about 1.3. Air is fed to the catalyst regeneration zone which is maintained at conditions to combust at least a portion of the carbonaceous catalyst deposit material, e.g., temperature of 1000°F. to 1100°F. and average catalyst residence time of about 50 minutes.

After a period of time in operation, it is determined that the catalyst mixture according to the present invention is effective both to promote toluene disproportionation in the reaction zone and to promote the oxidation of carbon monoxide to carbon dioxide in the regeneration zone. The catalyst mixture of this invention is found to provide improved results, e.g., improved carbon monoxide

oxidation catalytic activity stability while having substantially no deleterious effect on the hydrocarbon conversion in the reaction zone.

5 *EXAMPLE IV*

Example I is repeated, except that the alumina-based spheres include about 7% by weight of a crystalline aluminosilicate known to be catalytically active to promote
10 hydrocarbon conversion.

EXAMPLE V

Example III is repeated except that the discrete entities produced in Example I are replaced by the discrete entities of Example
15 IV. After a period of time in toluene disproportionation-catalyst regeneration service, this catalyst mixture is shown to be effective to promote both toluene disproportionation in the reaction zone and
20 carbon monoxide oxidation in the regeneration zone.

EXAMPLES VI AND VII

Examples II and V are repeated except that the catalyst mixtures are used to crack
25 a petroleum derived gas oil fraction, a combined fresh feed and recycle stream, in the moving catalyst bed reaction-regeneration system. The fresh gas oil fraction boils in the range of 400°F. to 1000°F. and is
30 substantially hydrocarbon in nature, containing minor amounts of sulfur and nitrogen as contaminants. Conventional hydrocarbon cracking and catalyst regeneration conditions are employed in the reaction zone
35 and regeneration zone, respectively.

The catalyst mixtures are found to be effective to promote hydrocarbon cracking and to promote carbon monoxide oxidation. Such hydrocarbon cracking operation provides improved results, e.g., prolonged
40 carbon monoxide oxidation catalytic activity while providing for effective hydrocarbon cracking catalytic activity.

EXAMPLE VIII

The discrete entities produced in Example II are intimately comingled with solid particles of commercially available hydrocarbon cracking catalyst similar to that used
50 in Example III except that the substantially all, by weight, of the particles have diameters in the range of 20 microns to 150 microns. The hydrocarbon cracking catalytic activity of such particles is equilibrated by service in a conventional
55 commercial fluid-bed catalyst cracking (FCC) unit. The resulting catalyst mixture includes 5 parts by weight of discrete entities and 95 parts by weight of the solid particles.

This catalyst mixture is used to crack a petroleum derived gas oil stream, similar to that described in Examples VI and VII, to lower boiling hydrocarbons in a conventional FCC unit.

65 Briefly, such unit involves two vessels

in at least limited fluid communication with each other. One vessel serves as a reaction zone. Hydrocarbon feedstock and catalyst particles are fed to the reaction zone at hydrocarbon cracking conditions. At least
70 a portion of the hydrocarbon cracking occurs in this reaction zone, where the catalyst and hydrocarbon form a fluid phase or bed.

Catalyst and hydrocarbon are continuously drawn from the reaction zone. The hydrocarbon is sent for further processing, distillation and the like. Catalyst, stripped of hydrocarbon, flows to the other vessel, catalyst regeneration zone, where it
80 is combined with air at proper conditions to combust at least a portion of the carbonaceous deposits from the catalyst formed during the hydrocarbon cracking reaction. The catalyst and vapors in the
85 regeneration zone form a fluid phase or bed. Catalyst is continuously removed from the regeneration zone and is combined with the hydrocarbon feedstock prior to being fed to
90 the reaction zone.

The weight ratio of catalyst particles to total (fresh plus recycle) hydrocarbon feed entering the reaction zone is about 8 to 1. Other conditions within the reaction zone
95 include:

Temperature, °F.	930	
Pressure, psig	8	
WHSV	15	

Such conditions result in about 70% by volume conversion of the gas oil feedstock to products boiling at 400°F. and below.

The catalyst particles from the reaction zone include about 1.5% by weight of carbonaceous deposit material which is at least partially combusted in the regeneration
105 zone. Air, in an amount so that amount of oxygen in the regeneration zone is about 1.15 times the amount theoretically required to completely combust this deposit material, is heated to the desired temperature before being admitted to the regeneration
110 zone. Conditions within the regeneration zone include:

Temperature, °F.	1150	
Pressure, psig.	8	115
Average Catalyst Residence Time, min.	12	

After a period of time, the catalyst is shown to remain effective to promote both hydrocarbon cracking in the reaction zone and carbon monoxide oxidation in the
120 regeneration zone.

The hydrocarbon feedstock employed in this Example is a sulfur contaminated hydrocarbon feedstock. Fresh hydrocarbon
125 feedstocks, e.g., petroleum derived gas oils, often contain 0.01% to 5% or more, preferably from 0.1% to 3%, by weight of sulfur. Such feedstocks form carbonaceous deposits on the catalyst which also contain sulfur.
130

During regeneration of such catalyst by contacting with an oxygen-containing gaseous stream, at least a portion of this deposit sulfur is oxidised to sulfur dioxide and, ordinarily, leaves the system with combustion flue gases. The presence of at least one platinum group metal component in the catalyst regeneration zone acts to promote the further oxidation of sulfur and sulfur-containing compounds to SO_3 . The SO_3 thus formed associates with the alumina of the discrete entities until such entities are placed in a hydrocarbon chemical reaction zone environment. Under such reaction zone conditions, at least a portion of this SO_3 is converted to H_2S which is removed from the reaction zone with the hydrocarbon conversion products.

EXAMPLE IX

Example VIII is repeated except that the discrete entities employed include about 7% by weight of a crystalline aluminosilicate known to be catalytically active to promote hydrocarbon cracking.

The present process provides improved properties and results. For example, the alumina-based discrete entities have outstanding carbon monoxide oxidation catalytic activity stability. That is, the time rate decline of carbon monoxide oxidation catalytic activity of the catalyst is reduced. Clearly the present process provides for improved hydrocarbon chemical conversion.

While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practised within the scope of the following claims.

In our copending application 4703/78, accepted as Serial No. 1 585 506, there is described and claimed a process for converting a hydrocarbon feedstock which comprises (1) contacting said feedstock in at least one reaction zone with a catalyst comprising solid particles capable of promoting the conversion of said feedstock at hydrocarbon conversion conditions to produce at least one hydrocarbon product and to cause deactivating carbonaceous material to be formed on said solid particles, thereby forming deposit-containing particles; (2) contacting said deposit-containing particles in at least one regeneration zone with an oxygen-containing vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of said solid particles and to form at least one carbonaceous deposit material combustion product; and (3) repeating steps (1) and (2) periodically; and in which said solid particles are substantially free of added metal components capable of promoting

carbon monoxide oxidation at the conditions of step (2) and said particles are circulated between said reaction zone and said regeneration zone in intimate admixture with a minor amount of discrete entities which are more attrition resistant than said solid particles and which comprise (A) a major amount by weight of a support at least a portion of which is capable of promoting hydrocarbon conversion at the conditions of step (1) and (B) a minor, catalytically effective, amount of at least one metal component disposed on at least a portion of said support, said metal component being capable of promoting the conversion of carbon monoxide to carbon dioxide at the conditions of step (2), thereby promoting the oxidation of carbon monoxide to carbon dioxide in said regeneration zone.

Our co-pending Application 7942599 (Serial 1 585 507) accepted as No. describes and claims a process for converting a sulfur-containing hydrocarbon feedstock which comprises (1) contacting said feedstock in at least one reaction zone with a catalyst comprising solid particles capable of promoting the conversion of said feedstock at hydrocarbon conversion conditions to produce at least one hydrocarbon product and to cause deactivating sulfur-containing carbonaceous material to be formed on said solid particles, thereby forming deposit-containing particles; (2) contacting said deposit-containing particles in at least one regeneration zone with an oxygen-containing vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material to thereby regenerate at least a portion of the hydrocarbon conversion catalytic activity of said solid particles and to form a regeneration zone flue gas containing at least one sulfur-containing carbonaceous deposit material combustion product; and (3) repeating steps (1) and (2) periodically, and in which the amount of sulfur in said regeneration zone flue gas is reduced by circulating said solid particles between said reaction zone and said regeneration zone in intimate admixture with a minor amount of discrete entities of a certain kind. In accordance with one aspect of the invention, the discrete entities comprise a major amount by weight of support and a minor, catalytically effective, amount by weight of at least one metal-containing component disposed on the support, the metal-containing component being capable of promoting the oxidation of carbon monoxide to carbon dioxide at carbon monoxide oxidising conditions, said discrete entities also being more attrition resistant than the solid particles and capable of promoting the oxidation of sulfur dioxide to sulfur

trioxide at the conditions of step (2), associating with sulfur trioxide at the conditions of step (2) and disassociating from sulfur trioxide at the conditions of step (1).

5 In accordance with another aspect of the invention, the discrete entities, differing in composition from that of the solid particles, comprise alumina and a catalytically effective amount of at least one platinum
10 group metal component disposed on the alumina and the discrete entities are capable of associating with sulfur trioxide at the conditions of step (2) and disassociating from sulfur trioxide at the conditions of
15 step (1).

WHAT WE CLAIM IS:—

1. A process for converting a hydrocarbon feedstock which comprises (1) contacting said feedstock in at least one
20 reaction zone with a catalyst comprising solid particles substantially free of added platinum group metal components and capable of promoting the conversion of said feedstock at hydrocarbon conversion con-
25 ditions to produce at least one hydrocarbon product and to cause deactivating carbonaceous material to be formed on said solid particles, thereby forming deposit-containing particles; and (2) contacting said deposit-
30 containing particles in at least one regeneration zone with an oxygen-containing vaporous medium at conditions to combust at least a portion of said carbonaceous deposit material to thereby regenerate at
35 least a portion of the hydrocarbon conversion catalytic activity of said solid particles and to form at least one carbonaceous deposit material combustion product; and (3) repeating steps (1) and (2) periodically, and
40 in which there are circulated between said reaction zone and said regeneration zone in intimate admixture with said solid particles, a minor amount of discrete entities comprising (A) a major amount by weight of
45 alumina and (B) a minor, catalytically effective amount of at least one platinum group metal component disposed on said alumina, said metal component being capable of promoting the oxidation of carbon monoxide
50 to carbon dioxide at the conditions of step (2), thereby promoting the oxidation of carbon monoxide to carbon dioxide in said regeneration zone.

2. A process as claimed in claim 1
55 wherein said platinum group metal component is present in an amount of 0.05 ppm to 1% by weight of the discrete entities, calculated as elemental metal.

3. A process as claimed in claim 2
60 wherein said platinum group metal com-

ponent is present in an amount of 0.05 ppm to 1000 ppm by weight of the total discrete entities, calculated as elemental metal.

4. A process as claimed in any one of claims 1 to 3 wherein said platinum group
65 metal component comprises a metal selected from the group consisting of platinum, palladium, and mixtures thereof.

5. A process as claimed in any one of claims 1 to 4 wherein the hydrocarbon
70 conversion is carried out in the substantial absence of added free molecular hydrogen.

6. A process as claimed in any one of claims 1 to 5 wherein said conversion com-
75 prises hydrocarbon cracking.

7. A process as claimed in any one of claims 1 to 6 wherein said discrete entities contain at least 70% by weight of alumina.

8. A process as claimed in claim 7 wherein said discrete entities contain at least
80 90% by weight of alumina.

9. A process as claimed in any one of claims 1 to 8 in which the alumina of said discrete entities has a surface area of
85 $25\text{m}^2/\text{gm}$ to $600\text{m}^2/\text{gm}$.

10. A process as claimed in any one of claims 1 to 9 wherein the alumina of said discrete entities is gamma alumina.

11. A process as claimed in any one of claims 1 to 9 wherein the alumina of said
90 discrete entities is derived from hydrous alumina predominating in alumina trihydrate, alumina monohydrate, amorphous hydrous alumina and mixtures thereof.

12. A process as claimed in any one of
95 claims 1 to 11 wherein said discrete entities further comprise a minor, catalytically effective amount of at least one material selected from silica, zirconia, magnesia and crystalline aluminosilicates capable of pro-
100 moting hydrocarbon conversion at the conditions of step (1).

13. A process as claimed in any one of claims 1 to 12 wherein the relative amounts of said solid particles and said discrete
105 entities are in the range of 80 parts to 99 parts and 20 parts to 1 part by weight, respectively.

14. A process as claimed in claim 13 wherein the relative amounts of said solid
110 particles and said discrete entities are in the range of 90 parts to 99 parts and 10 parts to 1 part by weight, respectively.

15. A process as claimed in any one of claims 1 to 14 wherein said solid particles
115 comprise a catalytically effective amount of at least one crystalline aluminosilicate.

16. A process as claimed in any one of claims 1 to 15 wherein the compositions of said solid particles and said discrete
120

entities minus said platinum group metal component are substantially the same.

17. A process as claimed in any one of claims 1 to 16 wherein said conversion 5 comprises hydrocarbon cracking and said solid particles are fluidisable.

18. A process as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.

10 19. A process as claimed in claim 1, sub-

stantially as illustrated in any one of the Examples.

20. Hydrocarbon feedstock when converted by the process claimed in any one of claims 1 to 19.

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MATHYS & SQUIRE,
Chartered Patent Agents,
10 Fleet Street,
London EC4Y 1AY.
Agents for the Applicants.