Patented Apr. 7, 1942

2,278,590

UNITED STATES PATENT OFFICE

2,278,590

CATALYTIC CRACKING OF HYDROCARBONS

Robert F. Ruthruff, Chicago, Ill.

No Drawing. Application October 20, 1939, Serial No. 300,390

18 Claims. (Cl. 196—52)

This invention relates to improved catalysts for the conversion of hydrocarbons of higher boiling point into hydrocarbons of lower boiling point.

The thermal conversion of hydrocarbons of higher boiling point into hydrocarbons of lower boiling point and more particularly into hydrocarbons in the motor fuel boiling range is well known in the art. Such thermal conversion processes suffer from many disadvantages; among these may be mentioned the comparatively low octane rating of the motor fuel produced and the high production of undesirable products, such as gas and tar, having little commercial value. These and other disadvantages have led to the development of various catalytic processes for the conversion of hydrocarbons of higher boiling range into hydrocarbons of lower boiling range and more particularly into hydrocarbons in the motor fuel boiling range. In comparison with thermal processes, the motor fuel produced by the catalytic conversion of higher boiling hydrocarbons is of much higher octane rating, the gas production is appreciably lower, and the production of material with a higher carbon-to-hydrogen ratio than that of the higher boiling hydrocarbon charge is much decreased.

As contact agents for catalyzing the conversion of higher boiling hydrocarbons into hydrocarbons of lower boiling point such materials as clays and synthetic silica-alumina complexes have been suggested. While these contact agents are fairly satisfactory, they suffer from numerous disadvantages. For example, while the gasoline-to-gas ratio in the catalytic conversion of higher boiling hydrocarbons to hydrocarbons of lower boiling point is higher than in thermal conversion processes, from a theoretical standpoint even greater ratios are obtainable. Likewise, while in catalytic conversion the yield of material having a higher carbon-to-hydrogen ratio than the charge is less than in thermal processes, here again further improvements are to be expected from a theoretical standpoint. The carbon-hydrogen ratio of a cracked gasoline is very nearly the same as that of a virgin gas oil. Accordingly, from a theoretical standpoint, the conversion of this higher boiling hydrocarbon mixture into the lower boiling should proceed almost quantitatively with the simultaneous production of little or no material other than the major product. That this does not occur in either thermal or catalytic conversion processes is well known to those familiar with the art. Furthermore, all catalysts known to date for promoting the conversion of higher boiling hydrocarbons to hydrocarbons of lower boiling point decline in activity more or less rapidly with use, due to the deposition of carbon or carbonaceous residues on the surfaces of said catalysts. This necessitates the periodic regeneration of the contact agents employed, this being accomplished usually by burning the accumulated deposits from the surfaces of said contact agents by means of air or dilute air. With catalysts described in the prior art, for example, clays and synthetic silica-alumina complexes, this regeneration must be carried out with extreme care, since these contact agents suffer a permanent decline in activity if heated above certain temperatures. This necessitates elaborate precautions during the regeneration cycle and complicated apparatus for accomplishing revivification without injury to the contact agent. In addition, the contact agents described in the prior art are quite sensitive to water vapor, especially at high temperatures. This necessitates the elimination of water vapor from regeneration gases prior to passage over the catalyst and seriously limits the amount of steam that may be used in the catalytic conversion step to aid in vaporizing the hydrocarbon charge. My improved catalyst for the conversion of hydrocarbons of higher boiling point to hydrocarbons of lower boiling point does not exhibit the disadvantages shown by contact agents described in the prior art or exhibits these disadvantages to a less marked degree.

One object of my invention is to provide an improved contact agent for the conversion of hydrocarbons of higher boiling point to hydrocarbons of lower boiling point. A further object of my invention is to provide a contact agent for the conversion of hydrocarbons of higher boiling point to those of lower boiling point, the use of which results in a high production of desirable conversion products and a low production of undesirable products. Another object of my invention is to provide a contact agent for the conversion of hydrocarbons of higher boiling point into hydrocarbons of lower boiling point, said contact agent showing improved thermal stability in comparison with hitherto known contact agents for the purpose. An additional object of my invention is to provide a contact agent for the conversion of hydrocarbons of higher boiling point to hydrocarbons of lower boiling point, said contact agent exhibiting increased resistance to deterioration in the presence of steam in comparison with hitherto known contact agents.

Other objects of this invention will become evident from the following description.

My improved catalyst for the conversion of hydrocarbons of higher boiling point into hydrocarbons of lower boiling point is a synthetic material which is believed to be magnesium silicate containing more or less water of hydration. The desired material is made by treating a natural or synthetic alkaline earth silicate in a physical form exhibiting large specific surface with a solution containing a magnesium salt until substantially complete base exchange has occurred, following which the resulting solid is separated from the mother liquor, is washed and then converted to the desired physical form prior to use as a contact agent.

The alkaline earth silicate employed in the practice of my invention may be a synthetic material made, for example, by interaction of a solution of a salt of an alkaline earth metal with a solution of a soluble silicate or by fusing or otherwise treating silica with an alkaline earth salt, oxide or hydroxide. In addition, naturally occurring alkaline earth silicates may be employed. While from the standpoint of convenience and expense a simple alkaline earth silicate is usually employed, nevertheless complex alkaline earth silicates can be substituted therefor. In the formation of alkaline earth silicates in the wet way, there is no apparent advantage of forming other than a simple silicate. When an alkaline earth silicate is prepared in the dry way, it is at times advantageous to form a complex alkaline silicate for reasons that will be mentioned hereafter. Obviously, if natural silicates are employed these may be simple or complex, depending upon the nature of the natural deposit utilized. It should be noted that natural alkaline earth silicates practically without exception contain more or less magnesium, which apparently has no adverse effect on the use of such minerals as raw materials in the practice of this invention. For base exchange with a solution of a magnesium salt it is essential that the alkaline earth silicate, whether synthetically prepared or from a natural source, be in a physical form exhibiting high specific surface in order that the base exchange reaction may proceed rapidly and to substantial completion. As synthetic silicates made by the interaction of a solution of a salt of an alkaline earth metal with a solution of a soluble silicate are obtained directly in the desired physical form, this method is generally preferred as a step in the manufacture of my improved catalyst.

A specific example of one method of preparing my improved catalyst will be found in the following Example 1.

Example 1.—To commercial water glass (sodium silicate solution), preferably diluted with four or more volumes of water, is added slowly, with stirring, a solution containing an excess of calcium ion, calcium chloride for example. Preferably the volume of the calcium salt solution is approximately equal to the volume of the diluted water glass solution. The amount of calcium salt required cannot be specified exactly as this varies with the composition of the water glass employed, the precipitating conditions, and other factors. As is well known to those skilled in the art, various grades of water glass have widely differing compositions. For example, one extensively used commercial grade of water glass contains about 28.5% silica and about 8.85% sodium oxide, the silica-sodium oxide ratio being 3.22 to 1. Grades having ratios greater or less than that quoted are also marketed. In general, I prefer to use water glass having a silico-sodium oxide ratio of 3 to 1 or less. The amount of calcium salt required, which varies with the silico-sodium oxide ratio of the particular grade of water glass employed, is greater than that required theoretically to react with the sodium oxide in accord with the equation

$$Na_2O+CaCl_2\rightarrow 2NaCl+CaO$$

and equal to or less than that required to react with the silica in accord with the theoretical equation $CaO+SiO_2\rightarrow CaSiO_3$. In general, it is best to determine experimentally the calcium ion requirements for the grade of water glass employed, adding the calcium-containing solution slowly with agitation to the dilute water glass solution until the supernatant liquid shows a distinct and non-fugitive test for the calcium ion. The resulting precipitate of calcium silicate is separated from the mother liquor by any suitable means and is then washed salt-free. The product is obtained in the form of a precipitate having an extremely large specific surface and is hence eminently suited for use in the base exchange reaction that follows. For base exchange, the resulting precipitate is heated, preferably with stirring, in a solution containing a magnesium salt, for example magnesium chloride. The volume of the magnesium salt solution may conveniently be set approximately equal to that of the reaction mixture in which the precipitation of the calcium silicate occurred. In this way one vessel may, if desired, be used in the precipitation of the calcium silicate and for the base exchange reaction. The magnesium salt solution contains a slight excess of magnesium over that required for replacement of the calcium in the calcium silicate, although a large excess of magnesium may be used if desired. After boiling the agitated calcium silicate-magnesium salt solution slurry for a short period, for example one hour, the base exchange reaction is essentially complete, and accordingly the resulting solid is separated from the mother liquor by any suitable means, is washed salt-free, and is then worked up as will be described subsequently.

While in the above example the use of sodium silicate is specified, it is obvious that any soluble silicate, for example potassium silicate, will be equally suitable, the sodium silicate being selected on the basis of availability and cost. Similarly, any soluble calcium salt, for example the nitrate or bromide, can be used in place of the chloride. Also, slightly soluble calcium salts, such as the sulfate, can be employed if desired. For example, by agitating a dilute sodium silicate solution with finely divided calcium sulfate metathesis gradually occurs with the separation of calcium silicate. While in the example the addition of a calcium salt solution to diluted water glass is specified, equivalent results may be obtained by adding diluted water glass to calcium salt solution or by running the water glass and the calcium salt solutions simultaneously, with agitation, into a third vessel. Any sufficiently soluble magnesium salt may be employed in the base exchange. It should be pointed out, however, that the magnesium salt of an acid forming an insoluble precipitate with the calcium ion will result in the formation of a magnesium silicate contaminated with the resulting calcium salt. For example, when magnesium sulfate is employed, the resulting desired product is con-

taminated with calcium sulfate. It will be evident that in Example 1 the mother liquor obtained after base exchange of the calcium silicate precipitate with magnesium chloride solution consists essentially of a solution of calcium chloride. If desired, this solution may be sent back to the precipitator and interacted with additional water glass.

As is well known, water glass is prepared by fusing a mixture of high silica material such as sand or diatomaceous earth with soda ash at 1350–1450° C. or higher and dissolving the resulting glass in water. Because of the high temperatures required and the short life of the furnace linings, due to the severe operating conditions, water glass is much more expensive than would be expected on the basis of the raw materials used in its production. Water glass can be made at much lower temperatures by substituting caustic soda for soda ash, but the method is not economical due to the relatively high cost of caustic soda. In the present process, however, the water glass may, in effect, be made economically by use of caustic soda as the following Example 2 sets forth.

Example 2.—Finely divided sand or other high silica material, such as diatomaceous earth, is autoclaved with an aqueous suspension of calcium hydroxide containing a small amount of caustic soda. A satisfactory mixture is one containing 10 moles calcium hydroxide, 1 mole caustic soda, and 11 to 11.5 moles silica. The slurry is heated, preferably with agitation, for 1–2 hours under 20 to 40 atmospheres pressure. After cooling and releasing any residual pressure, a calcium silicate slurry in a solution containing a small amount of sodium silicate is obtained. The residual sodium silicate is reacted with an excess of a solution of a soluble calcium salt as described in Example 1, following which the resulting calcium silicate is separated from the mother liquor, washed, and base-exchanged as previously described. If desired, the small amount of caustic soda used may be omitted, but if this is done the hydrothermal reaction of the calcium hydroxide with the silica is quite slow.

A third method for preparing a magnesium silicate suitable for the purpose of this invention will now be described.

Example 3.—An approximately equimolecular mixture of calcium oxide and silica, preferably in a finely divided state, is brought to the liquid state by the application of heat. The resulting calcium silicate is then treated so as to increase the specific surface as much as possible. This may be accomplished, for example, by cooling the fused mass and then pulverizing. Or the hot fused mass may be dumped into a large volume of water to produce a preliminary granulation, following which the resulting material is pulverized. Or the fluid mass may be blown with air, steam, or other inert gas to convert the molten slag into a rock wool, which is then pulverized. The material resulting from any of these processes is then base-exchanged. To accomplish base exchange within a reasonable time, in the present instance quite severe conditions are necessary, due to the fact that the calcium silicate produced in accord with this example has a much lower specific surface than material made by precipitation. For this reason, the highly comminuted calcium silicate is made into a slurry with a solution containing an excess of a soluble magnesium salt (based on the calcium present), and the whole is autoclaved at elevated temperature and pressure for 1 to 2 hours. A reaction temperature of about 250° C. is suitable, and the reaction mixture is preferably stirred during treatment. After cooling, the solid is separated from the mother liquor, is washed, and may be worked up as described subsequently.

In this example it is evident that equivalents for quicklime may be substituted therefor, for example, calcium carbonate (limestone), calcium hydroxide, calcium nitrate, most calcium salts of organic acids, and the like. It has been found that dolomite (calcium magnesium carbonate) may be used in place of quicklime.

In place of preparing synthetic alkaline earth silicates as described in Example 3, natural alkaline earth silicate minerals may be employed, for example wollastonite. To confer a large specific surface on these minerals, they may be reduced mechanically to an extremely fine state of subdivision prior to base exchange or the minerals may be brought to a fluid state by the application of heat, following which the molten slag is treated as described in Example 3. As will be obvious to those skilled in the art, comminuted material prepared from natural alkaline earth silicates will not have the extremely large specific surfaces exhibited by alkaline earth silicates prepared synthetically in the wet way, and accordingly more strenuous base exchange conditions must be employed in treating these comminuted natural materials, employing, for example, the method outlined in Example 3.

If silicates are employed containing other than approximately equimolecular quantities of alkaline earth oxide and silica, it is advisable to add sufficient alkaline earth oxide or sufficient silica, as the case requires, to give a mixture for fusion having the two compounds in approximately equimolecular proportions. The same procedure is advisable if acidic or basic slags are employed.

The washed magnesium silicates prepared in accord with the teachings of this invention are further processed for the production of the final catalyst, the exact procedure followed depending on the conversion process to be employed. Processes for the catalytic conversion of higher boiling hydrocarbons into hydrocarbons of lower boiling point may conveniently be classified into three broad groups, as follows:

(*a*) *Fixed bed conversion processes.*—In these the higher boiling hydrocarbon charge, preferably in the vapor state, is passed through a vessel containing the contact agent. Periodically, the hydrocarbon charge is diverted to a second vessel containing contact agent, while the contact agent in the first vessel is regenerated by the removal of carbonaceous deposits from the surface thereof with air or dilute air, following which the charge is again passed therethrough.

(*b*) *Moving bed conversion processes.*—In these the higher boiling hydrocarbon charge, preferably in the vapor state, is passed through a vessel through which the contact agent is moving either continuously or intermittently. The contact agent discharged passes to another vessel in which regeneration occurs, this being accomplished by moving the contact agent through said vessel and contacting with air or dilute air. The contact material discharged from the regeneration vessel is then conveyed to the inlet of the reaction vessel.

(*c*) *Conversion processes with powdered contact agent.*—In these, the higher boiling hydrocarbon charge, preferably in the vapor state, is

passed through an elongated conduit, the (powdered) contact agent being suspended in the charge and moving with it. On leaving this first conduit, the hydrocarbons are separated from the contact agent, while the contact agent is suspended in air or dilute air and is passed through a second elongated conduit. Contact agent is separated from the suspending fluid after discharge from this second conduit, the thus regenerated and separated contact material then being mixed with the high boiling hydrocarbon charge for repassage through the first elongated conduit.

It is obvious that a highly pulverized contact agent is desirable for processes *c*, while contact material in the form of aggregates of reasonable size and strength is desirable for processes *a* and *b*. By simply drying the washed magnesium silicate made according to the teachings of this invention, a cake is obtained which is quite friable and easily pulverized to give a finely divided material eminently suited for processes *c*. For making the contact material into aggregates of appreciable size and strength, suitable for use in processes *a* and *b*, several procedures may be employed, some of them being described briefly below.

I. The contact agent after drying is pelleted in a pill machine, a binder being used if necessary.

II. The magnesium silicate is dried to a moisture content of 25–40% and then is passed through an extrusion machine. The resulting "spaghetti" is cut to form cylinders of the desired size either before or after final drying. If desired, the damp magnesium silicate cake may, prior to extrusion, be mixed with a suitable binding agent, clay for example.

III. A portion of the washed magnesium silicate cake is dried and is then mixed with the remaining undried cake to give a mixture of the proper moisture content for extrusion. If desired, during the mixing of the undried and dried cakes a suitable binder may be added.

In the application of this contact agent for the conversion of higher boiling hydrocarbons to hydrocarbons of lower boiling point, the hydrocarbon charge, preferably in the vapor state, may be passed over the material at atmospheric or elevated pressure and at temperatures of from 750° F. to 950° F. or higher, preferably in the temperature range 825–900° F. The charge may be passed at a rate of 1 to 2 volumes (liquid) of charge per volume of catalyst space per hour, more or less, depending upon the temperature, character of the charge, amount and character of the desired products, and other factors.

In one specific test, magnesium silicate was compared with a natural contact agent commonly employed for converting higher boiling hydrocarbons into hydrocarbons of lower boiling point. Under conditions where both contact agents gave the same conversion to motor gasoline, the magnesium silicate contact agent gave only 40% as much gas as the natural material and only 60% as much carbonaceous residue on the surface of the contact material. It is evident that my improved catalyst gives a high production of desirable conversion products and a low production of undesirable products. On continued use, the magnesium silicate contact prepared in accord with this invention showed little or no permanent decline in activity, this in spite of the fact that no particular pains were taken to control temperature during regeneration. In addition, steam could be added with the hydrocarbon charge or with the regenerating fluid without adverse effect.

Although the present invention has been described in connection with details or specific examples thereof, it is not intended that these shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

I claim:

1. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of an alkaline earth silicate.

2. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of an alkaline earth silicate of large specific surface.

3. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of a precipitated alkaline earth silicate of large specific surface.

4. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of a comminuted alkaline earth silicate of largs specific surface.

5. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of a fused alkaline earth silicate of large specific surface.

6. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium siilcate pseudomorph of a fused, comminuted alkaline earth silicate of large specific surface.

7. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of calcium silicate.

8. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of calcium silicate of large specific surface.

9. A method of converting higher boiling hy-

drocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of precipitated calcium silicate of large specific surface.

10. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of comminuted calcium silicate of large specific surface.

11. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of fused calcium silicate of large specific surface.

12. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with a magnesium silicate pseudomorph of fused, comminuted calcium silicate of large specific surface.

13. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion in contact at a cracking temperature with the material produced by forming in the aqueous phase an alkaline earth silicate of large specific surface by the interaction of a soluble salt of an alkaline earth metal with a soluble silicate, separating said alkaline earth silicate of large specific surface and subjecting said alkaline earth silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

14. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion in contact at a cracking temperature with the material produced by forming in the aqueous phase calcium silicate of large specific surface by the interaction of a soluble calcium salt with a soluble silicate, separating said calcium silicate of large specific surface and subjecting said calcium silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

15. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with the material produced by forming, in the aqueous phase, calcium silicate of large specific surface by the interaction of a soluble calcium salt with sodium silicate, separating said calcium silicate of large specific surface, and subjecting said calcium silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

16. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with the material produced by subjecting an alkaline earth hydroxide, an alkali metal hydroxide and silica to hydrothermal reaction to form an alkaline earth silicate of large specific surface and an alkali metal silicate, forming additional alkaline earth silicate of large specific surface by adding a soluble alkaline earth salt thereto, separating said alkaline earth silicate of large specific surface, and subjecting said alkaline earth silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

17. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with the material produced by subjecting calcium hydroxide, an alkali metal hydroxide and silica to hydrothermal reaction to form calcium silicate of large specific surface and an alkali metal silicate, forming additional calcium silicate of large specific surface by adding a soluble calcium salt thereto, separating said calcium silicate of large specific surface, and subjecting said calcium silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

18. A method of converting higher boiling hydrocarbons to hydrocarbons of lower boiling point comprising vaporizing the higher boiling hydrocarbons and passing the vapors for a time sufficient to effect the required conversion, in contact at a cracking temperature with the material produced by subjecting calcium hydroxide, sodium hydroxide and silica to hydrothermal reaction to form calcium silicate of large specific surface and sodium silicate, forming additional calcium silicate of large specific surface by adding a soluble calcium salt thereto, separating said calcium silicate of large specific surface, and subjecting said calcium silicate of large specific surface to hydrothermal base exchange with a soluble magnesium salt.

ROBERT F. RUTHRUFF.