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HIGH TEMPERATURE REACTIONS

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This invention relates to an improved method of performing high temperature hydrocarbon reactions. More particularly, this invention relates to an improved material for containing high temperature hydrocarbon reactions.

A common phenomenon associated with processes in which hydrocarbons are heated to high temperatures in a reactor, as, for example, to accomplish partial or controlled pyrolysis, is the formation of carbon. Formation of carbon results in a loss of useful product materials. Accumulation of carboin within reactors employed in hydrocarbon pyrolysis lowers efficiency and may be sufficient to entirely block flow within the reactor. Undesirable formation and subsequent accumulation of carbon within reactors employed in high temperature hydrocarbon processes has plagued the industry for years. Typical of the processes in which carbon formation poses a problem are pyrolysis reactions such as the pyrolysis of benzene and its homologues to form polyaryls, the pyrolysis of paraffins to form ethylene, propylene, butadiene, and the like, the pyrolysis of various alkyl-benzenes to produce styrene and its derivatives, the pyrolysis of various olefins, paraffines, or mixtures thereof to produce diolefins, and like pyrolysis reactions.

As a solution to the problem of carbon formation in high temperature hydrocarbon reactions, it has been suggested that reactors be constructed of steels which contain from about 11 to about 30 percent chromium and a maximum of about 1.5 percent nickel. Included within this composition range are steels of the AISI "400" series stainless steels. Examples of such AISI "400" series stainless steels and their nominal compositions (percent, balance iron) are as follows:

AISI	C Max.	Mn Max.	Si Max.	Cr	Ni Max.	P Max.	S Max.	Other
TP405	0.08	1.00	0.75	11.5-13.5	0.50	0.03-0.04	0.03	Al 0.10-0.30.
TP410	0.15	1.00	0.75	11.5-13.5	0.50	0.03-0.04	0.03	
TP430	0.12	1.00	0.75	14.0-18.0	0.50	0.03-0.04	0.03	
TP443	0.20	1.00	0.75	18.0-23.0	0.50	0.03-0.04	0.03	Cu 0.90-1.25.
TP446	0.20	1.50	0.75	23.0-30.0	0.50	0.03-0.04	0.03	N 0.10-0.25.

Although the use of AISI "400" series stainless steels for reactors solves the problem of carbon formation, another problem manifests itself. AISI "400" series stainless steels in general do not have particularly good mechanical properties (strength) at temperatures over about 550 degrees centigrade. Ordinarily, pyrolysis reactions, as contemplated by the present invention, are run at temperatures of from about 700 to about 900 degrees centigrade in order to obtain an efficient conversion of feed to the desired product, although certain materials may react at slightly lower temperatures. The temperature of the reactor metal may be more than 100 degrees centigrade higher than the reaction temperature in situations where the reaction is generally endothermic and heat must be supplied from outside the reactor as by a gas furnace or an electric heater.

A number of well known steels have good mechanical properties (strength) at temperatures above about 550 degrees centigrade as contemplated by the present invention. A substantial number of these high temperature steels contain nickel or cobalt usually in an amount greater than about 3 percent. It has been observed, however, that the presence of nickel or cobalt in a steel in excess of about 1.5 percent tends to catalyze carbon formation. Thus, while nickel or cobalt-containing steels have good high temperature properties, they are generally unsuitable for use as reactor materials in high temperature reaction processes.

We have discovered that the dual problems of high temperature strength and carbon fromation can be solved by providing a composite reactor having an AISI "400" series stainless steel surface exposed to the pyrolysis reaction, said AISI "400" series steel surface metallurgically bonded to a supporting steel having good high temperature strength such as a steel designated as one of the AISI "300" series. In this manner, benefit is obtained from the high temperature properties of the chromium-nickel steel, while maintaining carbon formation and accumulation at a minimum. Metallurgical bonding may be accomplished as by co-extrusion of the two metal portions while applying an appropriate amount of heat. Metallurgical bonding is a true molecular or atomic bonding between oxide-free surfaces of dissimilar metals.

Because of space considerations, reactors are usually fabricated of tubing of the desired size and length and which may be formed in a coil. Further, a plurality of reactor tubes may be manifolded to a header in order to give additional capacity. For this and other reasons, metallurgical bonding between reaction contacting surface and supporting metal is required.

Without metallurgical bonding between reaction contacting surface and support metal, fabrication of the reactor is usually beset by problems such as separation of the two component parts, or collapse of the inner reactor surface during bending operations. In use, non-metallurgically bonded composites tend to suffer from distortion due to differences in thermal expansion characteristics of the metals. Thermal distortion of a cyclic nature can cause eventual rupture of the reaction contacting surface, the support metal or both. When non-metallurgically bonded composite tubing, for example, is manifolded to a common header, bimetallic distortion tends to loosen and eventually destroy the joints.

A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, and are not to be construed to limit, the present invention.

Example 1

A steel tube 52 inches long and having an outer diameter of 4 inches was positioned vertically in a two zone electric furnace. The tube wall had an outer portion of AISI–TP304 [1] steel 0.270 inch thick metallurgically bonded to an inner portion of AISI–TP446 steel 0.030 inch thick. Saddles of a material which is resistant to heat and chemicals were used to pack the upper portion of the reactor tube, thereby providing additional vaporizing surface. The packed portion of the tube was maintained at about 400 degrees centigrade to insure full vaporization of the feed.

[1] AISI–TP304 steel has a nominal composition of 0.08 percent maximum carbon, 2.00 percent maximum manganese, from 0.03 to 0.04 percent maximum phosphorus, 0.03 percent maximum sulfur, 0.75 percent maximum silicon, from about 18 to about 20 percent chromium, from about 8 to about 11 percent nickel, and the balance iron.

With the unpacked zone of the reactor tube maintained at a temperature of about 800 degrees centigrade, benzene and steam were fed to the reactor at rates of about 425 and 450 grams per hour, respectively, for a period of about twenty hours. After removal of the steam, the product obtained contained about 9.5 percent by weight of diphenyl and terphenyls.

After discontinuance of the run, the unpacked reaction zone was examined for carbon formation and build up. No measurable quantity of carbon was found.

Example 2

Propylene and steam were fed to the reactor of Example 1 at rates of about 425 and 1100 grams per hour, respectively. Temperature of the unpacked reaction zone was varied from about 700 to about 850 degrees centigrade. At a reaction temperature of about 700 degrees centigrade a product containing about 1.6 percent by weight ethylene was obtained. When the temperature of the reaction zone was increased to about 850 degrees centigrade, the amount of ethylene in the product increased to about 33.7 percent by weight.

After about five hours of operation, no measurable quantity of carbon had formed or built up inside the reactor.

Example 3

Kerosene and steam were fed to the reactor of Example 1 at rates of about 420 and 1100 grams per hour, respectively. Temperature of the unpacked reaction zone was varied from about 750 to about 900 degrees centigrade. At a temperature of about 700 degrees centigrade, a product containing about 17.4 percent by weight ethylene was obtained. At temperatures of about 850 and 900 degrees centigrade, product containing about 33.7 and 30 weight percent ethylene, respectively, was obtained.

After about eight hours of operation, no measurable quantity of carbon had formed or accumulated within the reactor.

Example 4

Ethylbenzene and steam were fed to the reactor of Example 1 at rates of about 495 and 1100 grams per hour, respectively. Temperature of the unpacked reaction zone was varied from about 600 to about 900 degrees centigrade. The best conversion was obtained at a temperature of about 850 degrees centigrade, the product containing about 31.6 percent by weight styrene.

After about fourteen hours of operation, no measurable quantity of carbon had formed or accumulated in the reactor.

Example 5

A self regenerative catalyst of the potassium and chromium promoted Fe_2O_3 type was positioned in the previously unpacked reaction zone of the reactor used in the previous examples. Ethylbenzene and steam were fed to the reactor at rates of about 490 and 1100 grams per hour, respectively. The reaction zone (containing catalyst) was maintained at a temperature of about 570 degrees centigrade. A product containing about 44 percent by weight styrene was obtained.

After about 210 hours of operation no measurable quantity of carbon had formed or accumulated.

Example 6

To the catalyst-containing reactor of Example 5 were fed butene-1 and steam at rates of about 420 and 1200 grams per hour, respectively. The reaction zone was maintained at a temperature of about 600 degrees centigrade. Product containing about 19 percent by weight butadiene was obtained.

Inspection after about two and one-half hours of operation indicated that no measurable quantity of carbon had formed or accumulated.

Example 7

Using the reactor of Example 1, other high temperature hydrocarbon reactions, such as oxidation, synthesis, dehydration, and the like wherein a hydrocarbon is vaporized and subjected to high temperatures, may be performed with similar freedom from carbon formation in the reactor.

Various modifications may be made in the present invention without departing from the spirit or scope thereof, and it is to be understood that we limit ourselves only as defined in the appended claims.

We claim:

1. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 500 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel containing from about 11 to about 30 percent chromium and a maximum of about 1.5 percent nickel, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

2. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 500 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel selected from the groups consisting of those having AISI designations of TP405, TP410, TP430, TP443, and TP446, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

3. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 550 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel having the AISI designation TP405, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

4. In a method of performing high temperature reactions wherein hydrocarbons vapors are subjected to temperatures above 500 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel having the AISI designation TP410, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

5. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 550 degrees centigrade, the improvement which comprises carrying out the reation in a reactor having a reaction contacting surface of a steel having the AISI designation TP430, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

6. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 500 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel having the AISI designation TP443, such steel being metallurgically bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

7. In a method of performing high temperature reactions wherein hydrocarbon vapors are subjected to temperatures above 500 degrees centigrade, the improvement which comprises carrying out the reaction in a reactor having a reaction contacting surface of a steel having the AISI designation TP446, such steel being metallurgi-

cally bonded to a supporting second steel which has good strength at temperatures above about 550 degrees centigrade.

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