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(54) **ACTIVE COATING SYSTEM FOR  
REDUCING OR ELIMINATING COKE  
BUILD-UP DURING PETROCHEMICAL  
PROCESSES**

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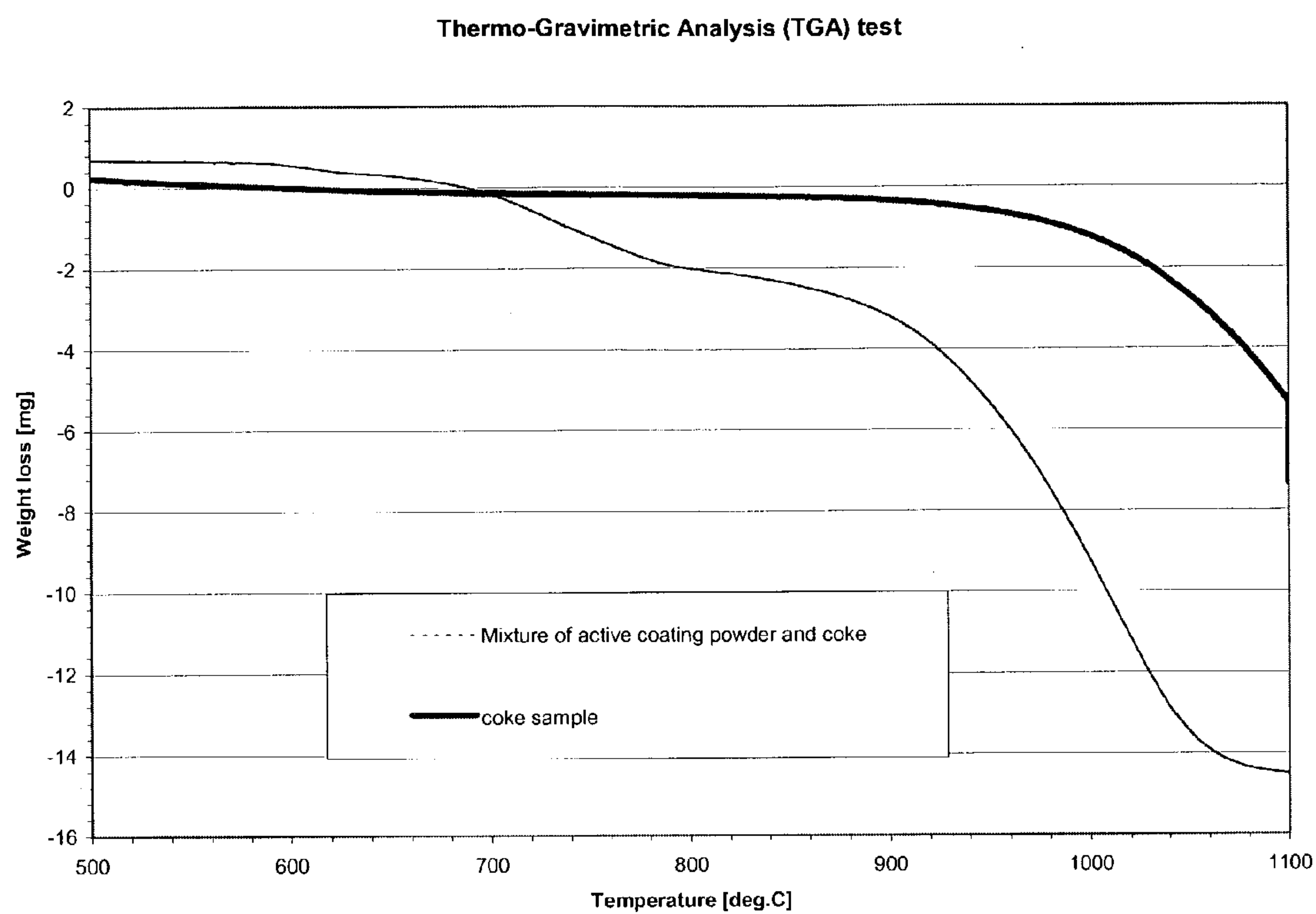
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(57) **ABSTRACT**

The invention relates to an active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component. The coating comprises a catalyst system and an adhesion/activation promoter. The catalyst system comprises at least a first compound and a second compound. The first compound is selected from one of the following groups of compounds: (a) a Group IA metal salt, (b) a Group IIA metal salt, and (c) a rare earth metal oxide, and the second compound is selected from a different group from the first compound. The adhesion/activation promoter comprises at least a first oxide and a second oxide. The first oxide is selected from one of the following groups of oxides: (d) a Group IIA oxide, (e) a Group IIIA oxide, and (f) a Group IVA oxide, and the second oxide is selected from a different group from the first oxide. In a preferred embodiment, the catalyst system comprises a Group IA metal salt, a Group IIA metal salt and a rare earth metal oxide, and the promoter comprises a Group IIA oxide, a Group IIIA oxide and a Group IVA oxide.

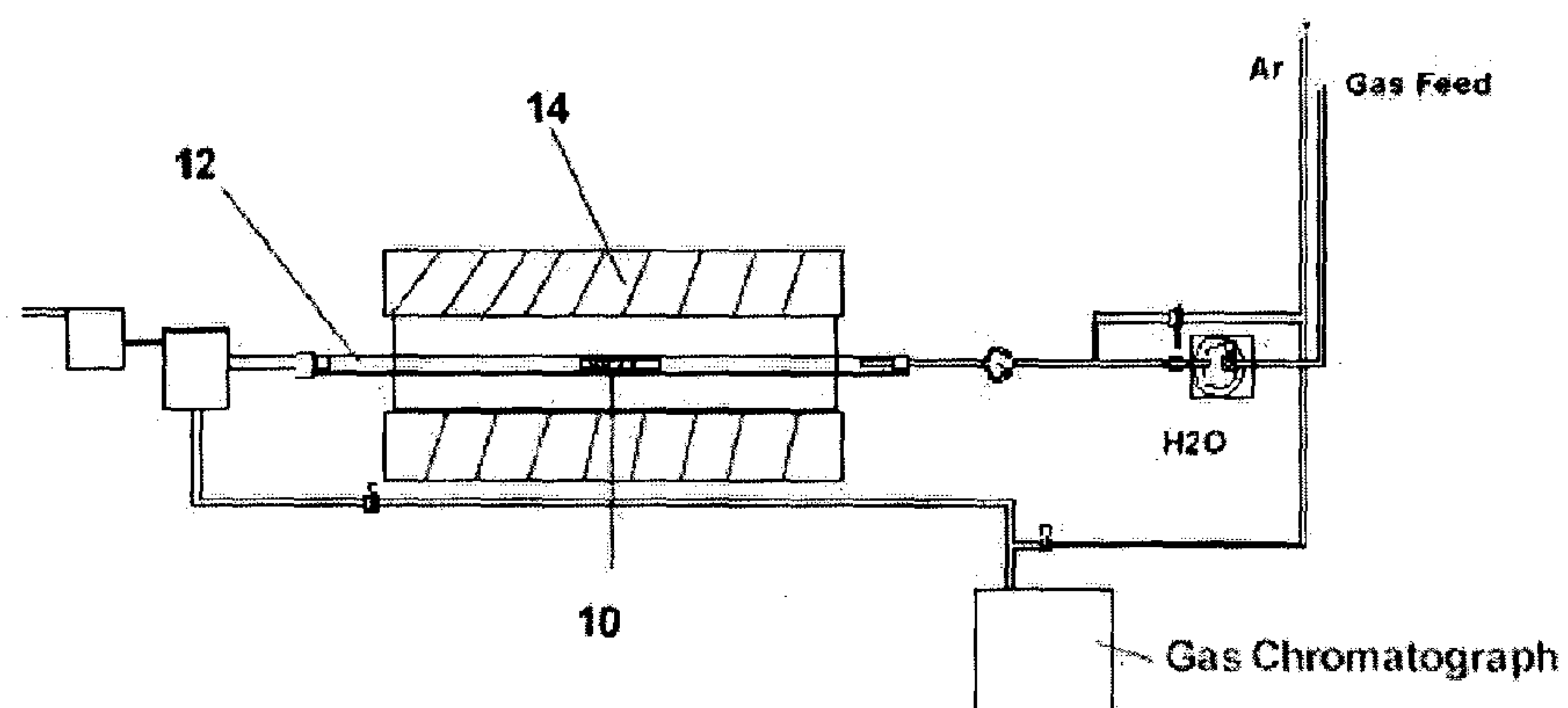
Also disclosed is a method for protecting the inner surfaces of reactor components, such as radiant tubes, fittings and reaction vessels, from coking and corrosion by coating the inner surfaces with the active coating.



**Figure 1**

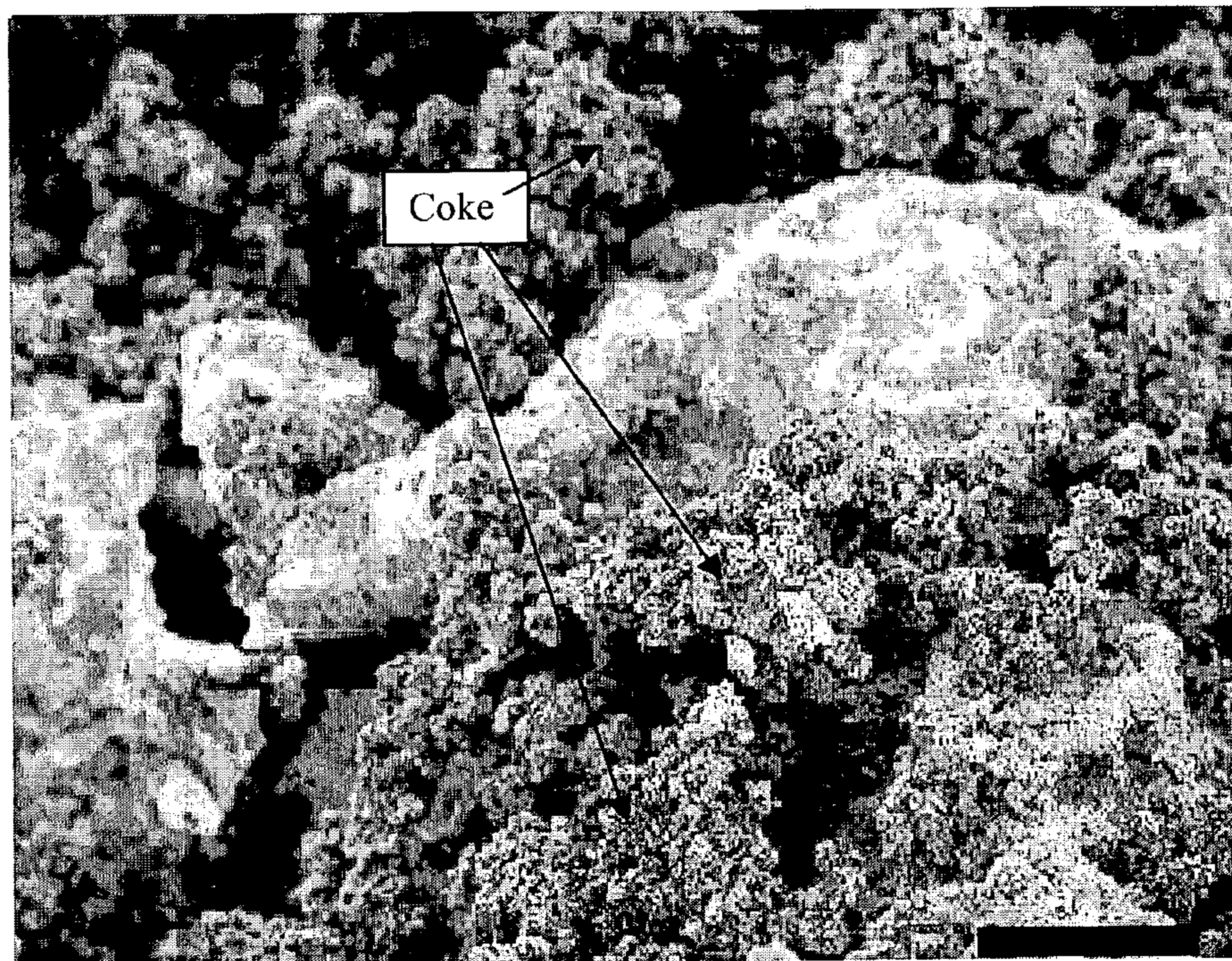
**TGA Test of a Coke Sample Mixed with Active Coating**

- Test atmosphere = Ethane/Steam 3:1
- T = 900°C



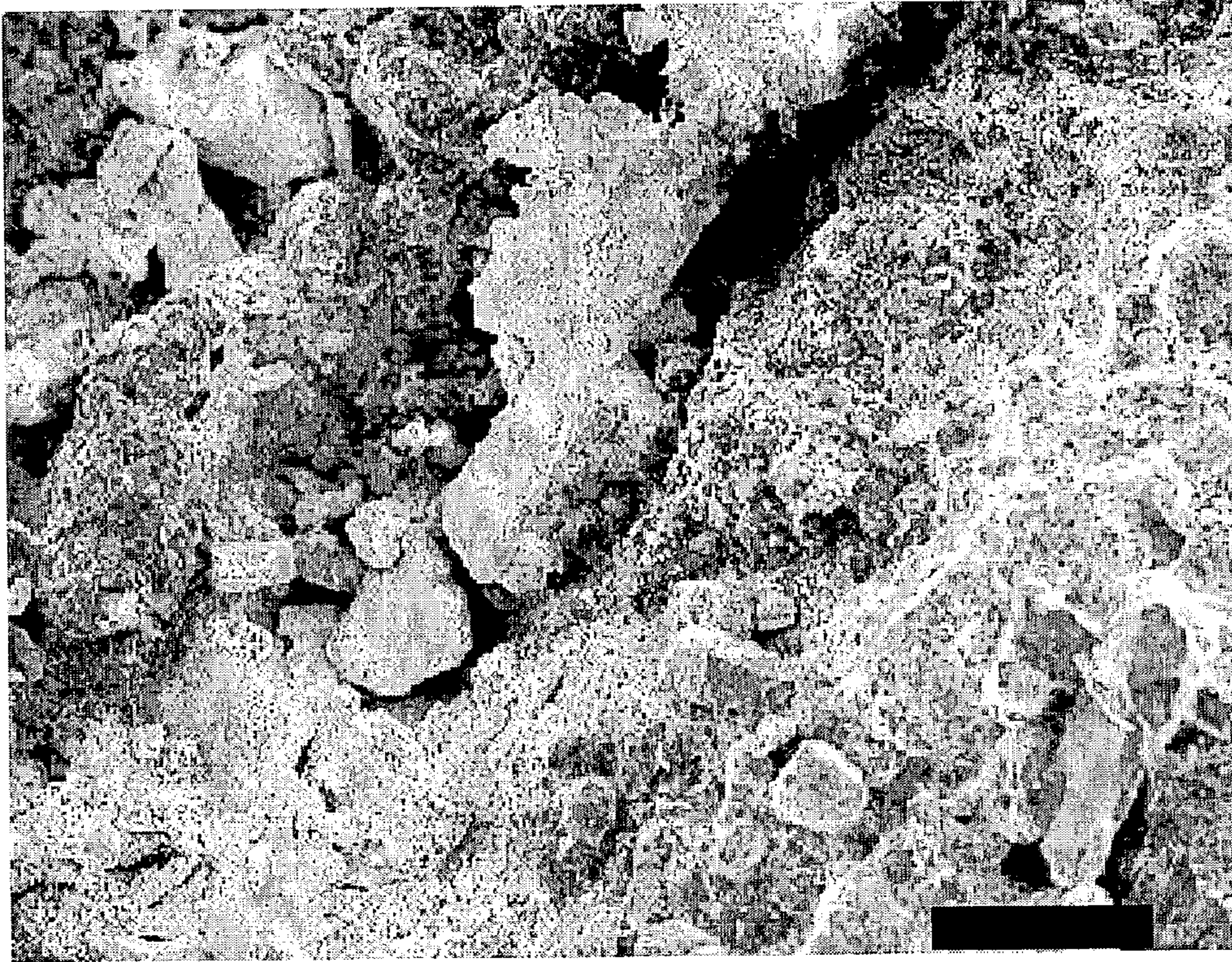
**Figure 2**  
**Sample Coking Test**





**Figure 3**  
**Commercial Coating after Coking Test**





**Figure 4**  
**Active Coating System after Coking Test**



## ACTIVE COATING SYSTEM FOR REDUCING OR ELIMINATING COKE BUILD-UP DURING PETROCHEMICAL PROCESSES

### FIELD OF THE INVENTION

[0001] The present invention relates to reducing or eliminating build-up of coke deposits on reactor components, such as a furnace, a tube fitting, a reaction vessel, and a radiant tube, used in petrochemical processes. More specifically, the present invention relates to an active coating and method to reduce or eliminate the build-up of coke deposits during petrochemical processes, such as hydrocarbon cracking processes.

### BACKGROUND OF THE INVENTION

[0002] Steam, catalytic cracking and pyrolysis of hydrocarbons to olefins, such as ethylene and propylene, are important processes in the petrochemical industry. Hydrocarbons such as ethane, propane, butane and naphtha are cracked in reactors, in the presence of steam, at temperatures of from about 800° C. to 850° C. in order to produce light olefins. The production volume of such processes is extremely large and therefore any small improvements in operating efficiency would be very economical and commercially advantageous.

[0003] One of the disadvantages of hydrocarbon cracking processes is the build-up of carbonaceous deposits (i.e. coke deposits) on inner surfaces of reactor components, for instance, inner radiant tube surfaces of furnace equipment. The amount of coke formed is dependent upon processing conditions such as feedstock, temperature and steam dilution. Ideally, coke build-up is in equilibrium with coke gasification which results in a steady-state coke layer on the surfaces of reactor components at a coverage of less than 100%. Unfortunately, the process conditions in the industry are such that coke build-up usually prevails.

[0004] During hydrocarbon cracking processes, the inner radiant tube surfaces become gradually coated with a layer of coke which raises the radiant tube metal temperature (TMT) and increases the pressure drop through radiant coils.

[0005] There are two types of processes that are responsible for coke build-up. One type of process is catalytic coking, which occurs on clean tube surfaces where high nickel and iron compositions catalyze the dehydrogenation of hydrocarbons at elevated temperatures. The metal surface is very coke-active and produces filamentous coke coverage. The second type of process is pyrolytic coking, which occurs predominantly in the gas phase and coke condenses on the inner surface of the tube or is trapped by the filamentous coke coverage formed from catalytic coking, and forms a dense coke scale.

[0006] In order to decoke reactor components, the reactor must be periodically shut down. Typically, the decoking is carried out by combustion of the coke deposits with steam/air at temperatures of up to 1000° C. Such decoking cycles are required approximately every 10 to 80 days, depending on the operation mode, and result in interruption of production since the reactor must be shut down. In addition, coke build-up adversely affects the physical characteristics of the reactor components, such as the radiant tubes, by deteriorating mechanical properties such as stress rupture, thermal fatigue, and ductility.

[0007] A variety of methods have been considered in order to overcome the disadvantages of coke build-up on reactor components, such as furnace surfaces. These approaches include:

[0008] metallurgy upgrade to alloys with increased chromium content of the metal substrates used in the furnaces;

[0009] adding additives such as sulfur, dimethyl sulfide (DMS), dimethyl disulfide (DMDs) or hydrogen sulfide to the feedstock;

[0010] increasing steam dilution of feedstock, and improved process control;

[0011] selectively pre-treating the inner surface of the coils;

[0012] vapor diffused aluminum enrichment;

[0013] inert surface coating; and

[0014] catalytic gasification of coke to produce CO/CO<sub>2</sub> and hydrogen.

[0015] International patent application WO 97/25145 describes a coating system comprising a metallic adhesion promoter and a catalytically active cover layer. The metallic adhesion promoter is first applied to a metal base body and a catalyst containing suspension is applied to the adhesion promoter. A mesh insert supports the coating inside the radiant tube. In order to maximize the active surface area, all internal surfaces of the radiant tubes and fittings are covered with inserts coated with the catalyst suspension. While this coating system initially indicated that considerable economic benefits could be expected with its use, problems related to the thermal contact between the mesh insert and the radiant tube precluded the commercial development of the system.

[0016] German Patent 243 647 A1 describes a method for production of a gasification catalyst material based on calcium aluminate and potassium pyro-vandate. An alternative approach to the deposition of the same type of catalyst has been described in International patent application WO 97/25146. The coating disclosed in this application is deposited directly on the tube surface by plasma spray, or sintered in place using an adhesion promoting binder.

[0017] While some of the aforementioned methods and systems have general use in the petrochemical industry, it is desirable to provide a system and method that obviates and mitigates the shortcomings of the prior art and successfully reduces or eliminates the build-up of coke deposits.

### SUMMARY OF THE INVENTION

[0018] In accordance with one aspect of the present invention, there is provided an active coating for protecting the internal surfaces of reactor components, such as a furnace, a tube fitting, a reaction vessel, and a radiant tube, to reduce or eliminate the build-up of coke and corrosion at elevated temperatures during, but not limited to, petrochemical processes such as ethylene production by pyrolysis of hydrocarbons or the reduction of oxide ores.

[0019] In accordance with another aspect of the present invention, there is provided an active coating for reducing or



eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

[0020] a catalyst system comprising at least a first compound and a second compound, said first compound being selected from one of the following groups of compounds: (a) a Group IA metal salt, (b) a Group IIA metal salt, and (c) a rare earth metal oxide, and said second compound being selected from a different group from the first compound; and

[0021] an adhesion/activation promoter comprising at least a first oxide and a second oxide, said first oxide being selected from one of the following groups of oxides: (d) a Group IIA oxide, (e) a Group IIIA oxide, and (f) a Group IVA oxide, and said second oxide being selected from a different group from the first oxide. Preferably, the ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight, more preferably, 1:3.

[0022] In accordance with another aspect of the present invention, there is provided an active coating wherein the catalyst system catalyzes the gasification of carbonaceous material and the promoter acts as a binder for the catalyst system and as an adhesive to adhere the catalyst system to the metal surface of the reactor component.

[0023] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the catalyst system comprises from about 60% to about 87% by weight of the first compound and from about 13% to about 40% by weight of the second compound based on the total weight of the catalyst system.

[0024] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the promoter comprises from about 20% to about 50% by weight of the first oxide and from about 50% to about 80% by weight of the second oxide based on the total weight of the promoter.

[0025] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the catalyst system comprises a third compound selected from any one of the groups: (a), (b) and (c).

[0026] In accordance with another aspect of the present invention, there is provided an active coating wherein the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide.

[0027] In accordance with another aspect of the present invention, there is provided an active coating wherein the Group IA metal salt is potassium carbonate, the Group IIA metal salt is magnesium aluminum oxide and the rare earth metal oxide is cerium oxide.

[0028] In accordance with yet another aspect of the present invention, the catalyst system comprises from about 20% to about 55% by weight of the first compound, from about 20% to about 40% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system. Preferably, the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide.

[0029] In accordance with yet another aspect of the present invention, the catalyst system comprises from about 30% to about 53% by weight of the first compound, from about 30% to about 34% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system.

[0030] In accordance with another aspect of the present invention, there is provided an active coating wherein the promoter comprises a third oxide selected from any one of the groups: (d), (e) and (f).

[0031] In accordance with another aspect of the present invention, there is provided an active coating wherein the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide.

[0032] In accordance with another aspect of the present invention, there is provided an active coating wherein the Group IIA oxide is barium oxide, the Group IIIA oxide is aluminum oxide and the Group IVA oxide is silicon oxide.

[0033] In accordance with another aspect of the present invention, there is provided an active coating wherein the promoter comprises from about 10% to about 40% by weight of the first oxide, from about 5% to about 50% by weight of the second oxide and from about 30% to about 50% by weight of the third oxide based on the total weight of the promoter. Preferably, the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide.

[0034] In accordance with another aspect of the present invention, there is provided an active coating wherein the promoter comprises from about 12% to about 36% by weight of the first oxide, from about 32% to about 48% by weight of the second oxide and from about 32% to about 42% by weight of the third oxide based on the total weight of the promoter.

[0035] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the catalyst system comprises from about 20% to about 55% by weight of the Group IA metal salt, from about 20% to about 40% by weight of the Group IIA metal salt and from about 13% to about 40% by weight of the rare earth metal oxide based on the total weight of the catalyst system and the promoter comprises from about 10% to about 40% by weight of the Group IIA oxide, from about 5% to about 50% by weight of the Group IIIA oxide and from about 30% to about 50% by weight of the Group IVA oxide based on the total weight of the promoter.

[0036] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the catalyst system comprises from about 20% to about 55% by weight of the Group IA metal salt, from about 20% to about 40% by weight of the Group IIA metal salt and from about 13% to about 40% by weight of the rare earth metal oxide based on the total weight of the catalyst system and the promoter comprises from about 12% to about 36% by weight of the Group IIA oxide, from about 32% to about 48% by weight of the Group IIIA oxide and from about 32% to about 42% by weight of the Group IVA oxide based on the total weight of the promoter.

[0037] In accordance with yet another aspect of the present invention, there is provided an active coating



wherein the catalyst system comprises from about 30% to about 53% by weight of the Group IA metal salt, from about 30% to about 34% by weight of the Group IIA metal salt and from about 13% to about 40% by weight of the rare earth metal oxide based on the total weight of the catalyst system and the promoter comprises from about 10% to about 40% by weight of the Group IIA oxide, from about 5% to about 50% by weight of the Group IIIA oxide and from about 30% to about 50% by weight of the Group IVA oxide based on the total weight of the promoter.

[0038] In accordance with yet another aspect of the present invention, there is provided an active coating wherein the catalyst system comprises from about 30% to about 53% by weight of the Group IA metal salt, from about 30% to about 34% by weight of the Group IIA metal salt and from about 13% to about 40% by weight of the rare earth metal oxide based on the total weight of the catalyst system and the promoter comprises from about 12% to about 36% by weight of the Group IIA oxide, from about 32% to about 48% by weight of the Group IIIA oxide and from about 32% to about 42% by weight of the Group IVA oxide based on the total weight of the promoter.

[0039] In accordance with another aspect of the present invention, there is provided an active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

[0040] a catalyst system comprising from about 20% to about 55% by weight of potassium carbonate, from about 20% to about 40% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system; and

[0041] an adhesion/activation promoter comprising from about 10% to about 40% by weight of barium oxide, from about 5% to about 50% by weight of aluminum oxide and from about 30% to about 50% by weight of silicon oxide based on the total weight of the promoter. Preferably, the ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight, more preferably, 1:3.

[0042] In accordance with another aspect of the present invention, there is provided an active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

[0043] a catalyst system comprising from about 30% to about 53% by weight of potassium carbonate, from about 30% to about 34% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system; and

[0044] an adhesion/activation promoter comprising from about 12% to about 36% by weight of barium oxide, from about 32% to about 48% by weight of aluminum oxide and from about 32% to about 42% by weight of silicon oxide based on the total weight of the promoter. Preferably, the ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight, more preferably, 1:3.

[0045] In accordance with another aspect of the present invention, there is provided a method for reducing or eliminating the build-up of coke deposits during a petrochemical process, comprising applying a slurry of the active coating to the metal surface of the reactor component, wherein the coating bonds thereto. The reactor component is a component that is susceptible to coke build-up thereon.

[0046] In yet another aspect of the present invention, the active coating starts gasifying the coke deposited thereon efficiently when about 3% of the active coating surface is covered with coke.

[0047] In accordance with a further aspect of the present invention, there is provided a method to reduce or eliminate coke build-up on a metal surface. The method comprises applying a layer of an active coating to a selected metal surface of a process component (e.g. a reactor component) which enhances thermal cracking of hydrocarbons and selectively increases the production rate of a desired product.

[0048] In accordance with another aspect of the present invention, the process components (e.g. reactor components) expected to be exposed during the thermal cracking of hydrocarbons are coated with a layer of the active coating, which reduces or eliminates the build-up of filamentous coke and catalyzes the gasification of the condensing pyrolytic coke.

[0049] According to yet another aspect of the present invention, there is provided a method to coat a layer of active coating on different elements of a reactor tube to reduce or eliminate coke build up during the thermal cracking process, wherein the coating provides a supply of catalytic centers during the surface erosion.

[0050] In accordance with another aspect of the present invention, the active coating used in such processes has the following characteristics:

[0051] enhances selective production of a desired product from the petrochemical process, with minimal negative effects on the selective production;

[0052] adheres to the reactor components and does not flake or delaminate at the operating temperature of the process;

[0053] does not undergo any substantial physical and chemical changes at the operating temperature; and

[0054] has the capability to bear a thermal shock effect present at normal operation.

[0055] Other features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from the detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0056] The present invention will become more fully understood from the detailed description given herein and



from the accompanying drawings, which are given by way of illustration only and do not limit the intended scope of the invention.

[0057] FIG. 1 shows Thermo-Gravimetric analysis (TGA) of a coke sample and of a sample of active coating, in accordance with the present invention, mixed with coke;

[0058] FIG. 2 is a schematic of an apparatus used to subject samples of active coating to hydrocarbon cracking;

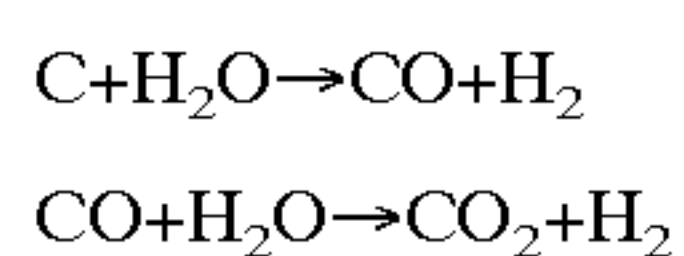
[0059] FIG. 3 is a Scanning Electron Microscope (SEM) image of a commercially available coating after undergoing a hydrocarbon cracking test using the apparatus of FIG. 2; and

[0060] FIG. 4 is a SEM image of the active coating of the present invention after undergoing a hydrocarbon cracking test using the apparatus of FIG. 2 simultaneously with the sample shown in FIG. 3.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0061] The present invention reduces or eliminates the build-up of coke deposits during petrochemical processes such as thermal cracking of hydrocarbons. The invention provides a novel active coating that may be applied to the metal surfaces of reactor components (understood by one of skill in the art to be any component used in a petrochemical process that is susceptible to coke formation thereon) and adhere thereto and acts to reduce or eliminate the build-up of coke deposits on such surfaces. The active coating is preferably used in processes that involve cracking of higher hydrocarbons within a pyrolysis furnace.

[0062] In order to reduce or eliminate the build-up of coke deposits on the metal surface of the reactor components, such as a furnace, a tube fitting, a reaction vessel, and a radiant tube, an active coating of the invention is applied thereto. The active coating is inert to catalytic coking and thus, inhibits filamentous coke formation. With respect to pyrolytic coking, the active coating reduces or eliminates coke build-up. In theory, the coke build-up resulting from pyrolytic coking is gasified by facilitating a water-gas shift reaction:



[0063] More specifically, coke, formed from pyrolytic coking, deposits on the surface of the active coating and gasification takes place according to the water-gas shift reaction (sic). Once about 3% of the active coating surface is covered with coke, the gasification reaction becomes efficient and the coke build-up is reduced or eliminated.

[0064] The active coating of the invention comprises a catalyst system and an adhesion/activation promoter. The catalyst system acts to catalyze the gasification of carbonaceous material (i.e. coke deposits). The adhesion/activation promoter acts as a binder for the catalyst system and as an adhesive to adhere the coating to the surface of the reactor component(s).

[0065] The catalyst system comprises at least two different compounds. The first compound is selected from one of the following groups: (a) an alkali metal salt (Group IA metal salt), (b) an alkaline earth metal salt (Group IIA metal salt),

and (c) a rare earth metal oxide (e.g. Sc, Y, Lu and lanthanides). The second compound is selected from a group other than the group from which the first compound was selected. For example, in a two compound catalyst system, if the first compound is chosen from the Group IIA metal salt group, the second compound has to be chosen from either the Group IA metal salt group or the rare earth metal oxide group.

[0066] The catalyst system may also comprise three or more compounds. If the catalyst system comprises three compounds, the first and second compounds are selected from different groups as described above and the third compound may be selected from any one of the three groups: (a), (b) and (c). In one embodiment of the three compound catalyst system, the first compound may be the Group IA metal salt, the second compound may be the Group IIA metal salt, and the third compound may be another Group IA metal salt. In another embodiment of the three compound catalyst system, the first compound may be the Group IA metal salt, the second compound may be the Group IIA metal salt, and the third compound may be the rare earth metal oxide. In a preferred embodiment of the catalyst system, the Group IA metal salt is potassium carbonate, the Group IIA metal salt is magnesium aluminum oxide and the rare earth metal oxide is cerium oxide.

[0067] The anion of the Group IA and Group IIA metal salts used in the catalyst system may be selected from the group consisting of a carbonate anion and an aluminate anion.

[0068] The adhesion/activation promoter comprises at least two different oxides. The first oxide is selected from one of the following groups: (d) a Group IIA oxide (e.g. barium oxide), (e) a Group IIIA oxide (e.g. aluminum oxide), and (f) a Group IVA oxide (e.g. silicon oxide). The second oxide is selected from a group other than the group from which the first compound was selected. For example, with respect to a promoter that comprises two oxides, if the first oxide is chosen from the Group IIA oxide group, the second oxide has to be chosen from either the Group IIIA oxide group or the Group IVA oxide group.

[0069] The promoter may also comprise three or more oxides. If the promoter comprises three oxides, the first and second oxides are selected from different groups as described above and the third oxide may be selected from any one of the three groups: (d), (e) and (f). In one embodiment of the three oxide promoter, the first oxide may be the Group IIA oxide, the second oxide may be the Group IIIA oxide, and the third oxide may be another Group IIA oxide. In another embodiment of the three oxide promoter, the first oxide may be the Group IIA oxide, the second oxide may be the Group IIIA oxide, and the third oxide may be the Group IVA oxide. In a preferred embodiment of the adhesion/activation promoter, the Group IIA oxide is barium oxide, the Group IIIA oxide is aluminum oxide and the Group IVA oxide is silicon oxide.

[0070] The ratio of the catalyst system to the adhesion/activation promoter may be from about 1:1 to about 1:5 based on weight, preferably, 1:3.

[0071] In another embodiment of the catalyst system, the catalyst system comprises two different compounds. The catalyst system comprises from about 60% to about 87% by



weight of the first compound and from about 13% to about 40% by weight of the second compound based on the total weight of the catalyst system. Preferably, the first compound is the Group IA metal salt and the second compound is the rare earth metal oxide. More preferably, the Group IA metal salt is potassium carbonate and the rare earth metal oxide is cerium oxide.

[0072] In another embodiment of the promoter, the promoter comprises two different oxides. The promoter comprises from about 20% to about 50% by weight of the first oxide and from about 50% to about 80% by weight of the second oxide based on the total weight of the promoter. Preferably, the first oxide is the Group IIA oxide and the second oxide is the Group IVA oxide. More preferably, the Group IIA oxide is barium oxide and the Group IVA oxide is silicon oxide.

[0073] With respect to a catalyst system comprising three different compounds, the catalyst system may comprise from about 20% to about 55% by weight of the first compound, from about 20% to about 40% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system. Preferably, the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide. In another embodiment, the catalyst system comprises from about 30% to about 53% by weight of the first compound, from about 30% to about 34% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system.

[0074] With respect to a promoter comprising three different oxides, the promoter may comprise from about 10% to about 40% by weight of the first oxide, from about 5% to about 50% by weight of the second oxide and from about 30% to about 50% by weight of the third oxide based on the total weight of the promoter. Preferably, the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide. In another embodiment, the promoter comprises from about 12% to about 36% by weight of the first oxide, from about 32% to about 48% by weight of the second oxide and from about 32% to about 42% by weight of the third oxide based on the total weight of the promoter.

[0075] Any combination of the promoter embodiments, as described, with the embodiments of the catalyst system, as described, are acceptable.

[0076] As is apparent to those skilled in the art, the combination of percentages of each component of the catalyst system or the promoter should total 100% by weight.

[0077] A preferred embodiment of the active coating of the present invention for reducing or eliminating the build-up of coke deposits comprises a catalyst system and an adhesion/activation promoter. The catalyst system comprises from about 20% to about 55% by weight of potassium carbonate, from about 20% to about 40% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system. The adhesion/activation promoter comprises from about 10% to about 40% by weight of barium oxide, from about 5% to about 50% by weight of aluminum

oxide and from about 30% to about 50% by weight of silicon oxide based on the total weight of the promoter. The ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight.

[0078] With respect to another embodiment, the catalyst system comprises from about 30% to about 53% by weight of potassium carbonate, from about 30% to about 34% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system and the adhesion/activation promoter comprises from about 12% to about 36% by weight of barium oxide, from about 32% to about 48% by weight of aluminum oxide and from about 32% to about 42% by weight of silicon oxide based on the total weight of the promoter. The ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight.

[0079] In one embodiment, the active coating may be prepared by thoroughly mixing the catalyst system, which comprises a mixture of potassium carbonate, magnesium aluminum oxide and cerium oxide, with the adhesion/activation promoter, which is a mixture of barium oxide, aluminum oxide and silicon oxide, in water or other suitable solvent to form a slurry. The ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight. The slurry is then applied to a desired surface of a reactor component. The amount of water present in the slurry is not critical. The amount of water is solely dependent on the mode of application of the coating, as is understood by one of skill in the art.

[0080] Without being bound by any theory, it is believed that the active coating alters the bond formation between a surface of the reactor component and the coke deposits, hence reducing or eliminating the build-up of coke deposits during the petrochemical process (i.e. the hydrocarbon cracking process). The active coating controls the build-up rate of coke deposits on the surface of the reactor components, such as reactor tubes. It is recognized that alkali metal compounds may be employed to catalyze the gasification of carbonaceous material. It is believed that when potassium carbonate and cerium oxide are present as the constituents in the coating, the coating reacts with the acidic carbonaceous species to form an alkali metal char "salt" which not only enhances the gasification process but also results in an increase in selective cracking to a target product.

[0081] The active coating of the present invention can be applied on the internal surfaces of various reactor components such as metal tubes and tubular substrates with varying complex shapes as a slurry, by sponging, painting, centrifuging, spraying and/or by dipping/fill-up techniques, as are well known to those of skill in the art. In particular, the active coating of the invention may be applied on reaction tubes and fittings used for steam cracking of hydrocarbons. The active coating may be applied with a thickness of from about 25 to 50 microns on the exposed surfaces. However, other thicknesses of active coatings can be contemplated for various applications.

[0082] The active coating of the invention provides an active surface that can be readily applied to reactor components such as metal surfaces to reduce or eliminate the build-up of filamentous coke and also catalyze the gasification of the condensing pyrolytic coke. The active coating has particular utility in the petrochemical industry.



[0083] The above disclosure generally describes the present invention. A more complete understanding can be obtained by reference to the following specific Examples. These Examples are described solely for purposes of illustration and are not intended to limit the scope of the invention. Changes in form and substitution of equivalents are contemplated as circumstances may suggest or render expedient. Although specific terms have been employed herein, such terms are intended in a descriptive sense and not for purposes of limitation.

#### EXAMPLE

[0084] An active coating powder was prepared by mixing the promoter prepared as set forth in Table 1 with the catalyst system set forth in Table 2.

TABLE 1

Promoter	Weight % (based on total weight of promoter)
SiO <sub>2</sub>	62.7
Al <sub>2</sub> O <sub>3</sub>	5.3
BaO <sub>2</sub>	32.0

[0085]

TABLE 2

Active Coating	Weight % (based on total weight of active coating and promoter)
Promoter from Table 1	25
K <sub>2</sub> CO <sub>3</sub>	25
CeO <sub>2</sub>	25
MgAl <sub>2</sub> O <sub>4</sub>	25

[0086] The powder sample of the active coating of Table 2 was mixed with an equal amount of coke and the activity of the mixture was tested using Thermo-Gravimetric Analysis (TGA). The sample temperature was ramped to 1000° C. at a rate of 10° C. per minute in a flow of nitrogen/steam=3:1 at atmospheric pressure. The sample weight loss was recorded as a function of time. As seen in FIG. 1, gasification of the coke present is accelerated when the active coating powder was mixed with the coke.

[0087] Samples of high temperature alloy, coated with a commercially available anti-coking coating were compared with samples coated with the active coating powder described above. The samples were coated via dipping in a water-based slurry of the anti-coking coating or the active coating powder. After drying at room temperature overnight, the samples were sintered at 1000° C. for one hour.

[0088] The samples of commercial coating and the active coating of the invention were subjected to a hydrocarbon-cracking test using the apparatus shown in FIG. 2. A sample 10 was placed inside a quartz reactor tube 12, positioned in a furnace 14 at 900° C., and subjected to flow of ethane gas diluted with steam at a ratio of 3:1 for one hour. The sample was then removed from the reactor and analyzed using SEM. The images of the sample surface after the coking test are shown in FIGS. 3 and 4. FIG. 3 shows that the surface of the commercially available coating has a deposited layer of amorphous coke illustrating that an inert surface does not

prevent condensation of pyrolytic coke from the gas phase. In contrast, FIG. 4 shows that the surface of the active coating of the present invention remains essentially clean (i.e. coke-free) under the same coking conditions, indicating that the deposited amorphous coke has been continuously gasified during the test.

[0089] The adherence of the active coating was tested on thermal shock by taking the samples out of the furnace at 1100° C., cooling down in air for 5 minutes at ambient temperature, and inserting them back into the furnace. The process was repeated 5 times and all tested samples demonstrated good adherence of the active coating to the high temperature alloy.

[0090] A three foot long tube with 1.5" ID was coated successfully with the active coating made as described with reference to Tables 1 and 2. The active coating was applied by lancing or spraying inside the rotating tube. The tube was dried slowly at room temperature while rotation continued and sintered in air at 1000° C. for 2 hours.

[0091] Various alternative coating compositions have been prepared and successfully applied as described above. The compositions are shown in Table 3.

TABLE 3

Alternative Active Coating Compositions						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	BaO <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	CeO <sub>2</sub>	MgAl <sub>2</sub> O <sub>4</sub>
Example 2	8	8	9	25	25	25
Example 3	10	10	4	30	20	26
Example 4	10	12	3	40	10	25
Example 5	20	20	10	15	20	15

[0092] The actual mechanism by which cerium, barium, magnesium, and potassium compounds activate the gasification process is not fully understood. Without being bound to any theory, it is believed that certain interactions between the different chemical species takes place and eventually results in transforming the poorly catalytic weak acid sites to strongly catalytic acid sites. It is further believed that the anion associated with potassium and the anion associated with Ce, Ba, and Mg exchange with each other to produce a complex that is reduced in the presence of carbon under gasification conditions. The net result is the creation of highly active gasification sites.

[0093] Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art that variations may be made thereto without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. An active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

a catalyst system comprising at least a first compound and a second compound, the first compound being selected from one of the following groups of compounds: (a) a Group IA metal salt, (b) a Group IIA metal salt, and (c) a rare earth metal oxide, and the second compound being selected from a different group from the first compound; and



an adhesion/activation promoter comprising at least a first oxide and a second oxide, the first oxide being selected from one of the following groups of oxides: (d) a Group IIA oxide, (e) a Group IIIA oxide, and (f) a Group IVA oxide, and the second oxide being selected from a different group from the first oxide.

2. The active coating of claim 1, wherein the catalyst system catalyzes the gasification of carbonaceous material and the promoter acts as a binder for the catalyst system and as an adhesive to adhere the catalyst system to the metal surface of the reactor component.

3. The active coating of claim 1, wherein the catalyst system comprises a third compound selected from any one of the groups: (a), (b) and (c).

4. The active coating of claim 1, wherein the promoter comprises a third oxide selected from any one of the groups: (d), (e) and (f).

5. The active coating of claim 3, wherein the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide.

6. The active coating of claim 4, wherein the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide.

7. The active coating of claim 1, wherein the Group IA metal salt is potassium carbonate, the Group IIA metal salt is magnesium aluminum oxide and the rare earth metal oxide is cerium oxide.

8. The active coating of claim 1, wherein the Group IIA oxide is barium oxide, the Group IIIA oxide is aluminum oxide and the Group IVA oxide is silicon oxide.

9. The active coating of claim 1, wherein a ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight.

10. The active coating of claim 9, wherein a ratio of the catalyst system to the adhesion/activation promoter is about 1:3 based on weight.

11. The active coating of claim 1, wherein the catalyst system comprises from about 60% to about 87% by weight of the first compound and from about 13% to about 40% by weight of the second compound based on the total weight of the catalyst system.

12. The active coating of claim 11, wherein the first compound is the Group IA metal salt and the second compound is the rare earth metal oxide.

13. The active coating of claim 12, wherein the Group IA metal salt is potassium carbonate and the rare earth metal oxide is cerium oxide.

14. The active coating of claim 1, wherein the promoter comprises from about 20% to about 50% by weight of the first oxide and from about 50% to about 80% by weight of the second oxide based on the total weight of the promoter.

15. The active coating of claim 14, wherein the first oxide is the Group IIA oxide and the second oxide is the Group IVA oxide.

16. The active coating of claim 15, wherein the Group IIA oxide is barium oxide and the Group IVA oxide is silicon oxide.

17. The active coating of claim 3, wherein the catalyst system comprises from about 20% to about 55% by weight of the first compound, from about 20% to about 40% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system.

18. The active coating of claim 17, wherein the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide.

19. The active coating of claim 17, wherein the catalyst system comprises from about 30% to about 53% by weight of the first compound, from about 30% to about 34% by weight of the second compound and from about 13% to about 40% by weight of the third compound based on the total weight of the catalyst system.

20. The active coating of claim 19, wherein the first compound is the Group IA metal salt, the second compound is the Group IIA metal salt and the third compound is the rare earth metal oxide.

21. The active coating of claim 4, wherein the promoter comprises from about 10% to about 40% by weight of the first oxide, from about 5% to about 50% by weight of the second oxide and from about 30% to about 50% by weight of the third oxide based on the total weight of the promoter.

22. The active coating of claim 21, wherein the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide.

23. The active coating of claim 21, wherein the promoter comprises from about 12% to about 36% by weight of the first oxide, from about 32% to about 48% by weight of the second oxide and from about 32% to about 42% by weight of the third oxide based on the total weight of the promoter.

24. The active coating of claim 23, wherein the first oxide is the Group IIA oxide, the second oxide is the Group IIIA oxide and the third oxide is the Group IVA oxide.

25. The active coating of claim 18, wherein the promoter comprises from about 10% to about 40% by weight of the Group IIA oxide, from about 5% to about 50% by weight of the Group IIIA oxide and from about 30% to about 50% by weight of the Group IVA oxide based on the total weight of the promoter.

26. The active coating of claim 18, wherein the promoter comprises from about 12% to about 36% by weight of the Group IIA oxide, from about 32% to about 48% by weight of the Group IIIA oxide and from about 32% to about 42% by weight of the Group IVA oxide based on the total weight of the promoter.

27. The active coating of claim 20, wherein the promoter comprises from about 10% to about 40% by weight of the Group IIA oxide, from about 5% to about 50% by weight of the Group IIIA oxide and from about 30% to about 50% by weight of the Group IVA oxide based on the total weight of the promoter.

28. The active coating of claim 20, wherein the promoter comprises from about 12% to about 36% by weight of the Group IIA oxide, from about 32% to about 48% by weight of the Group IIIA oxide and from about 32% to about 42% by weight of the Group IVA oxide based on the total weight of the promoter.

29. An active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

a catalyst system comprising from about 20% to about 55% by weight of potassium carbonate, from about 20% to about 40% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system; and



an adhesion/activation promoter comprising from about 10% to about 40% by weight of barium oxide, from about 5% to about 50% by weight of aluminum oxide and from about 30% to about 50% by weight of silicon oxide based on the total weight of the promoter.

**30.** The active coating of claim 29, wherein a ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight.

**31.** The active coating of claim 30, wherein a ratio of the catalyst system to the adhesion/activation promoter is about 1:3 based on weight.

**32.** An active coating for reducing or eliminating the build-up of coke deposits on a metal surface of a reactor component, the active coating comprising:

a catalyst system comprising from about 30% to about 53% by weight of potassium carbonate, from about 30% to about 34% by weight of magnesium aluminum oxide and from about 13% to about 40% by weight of cerium oxide based on the total weight of the catalyst system; and

an adhesion/activation promoter comprising from about 12% to about 36% by weight of barium oxide, from about 32% to about 48% by weight of aluminum oxide and from about 32% to about 42% by weight of silicon oxide based on the total weight of the promoter.

**33.** The active coating of claim 32, wherein a ratio of the catalyst system to the adhesion/activation promoter is from about 1:1 to about 1:5 based on weight.

**34.** The active coating of claim 33, wherein a ratio of the catalyst system to the adhesion/activation promoter is about 1:3 based on weight.

**35.** The active coating of claim 1, wherein the active coating is mixed with water or other suitable solvent to form a slurry.

**36.** The active coating of claim 35, wherein the slurry is applied to the metal surface of the reactor component.

**37.** The active coating of claim 36, wherein the slurry is applied by a method selected from the group consisting of sponging, painting, centrifuging, spraying and dipping fill-up technique.

**38.** The active coating of claim 36, wherein the reactor component is a component that is susceptible to coke formation thereon.

**39.** The active coating of claim 38, wherein the reactor component is selected from the group consisting of a furnace, a tube fitting, a reaction vessel, and a radiant tube.

**40.** A method for reducing or eliminating the build-up of coke deposits during a petrochemical process, comprising:

applying a slurry of the active coating of claim 1 to the metal surface of the reactor component, wherein the coating bonds thereto.

**41.** A method for reducing or eliminating the build-up of coke deposits during a petrochemical process, comprising:

applying a slurry of the active coating of claim 29 to the metal surface of the reactor component, wherein the coating bonds thereto.

**42.** A method for reducing or eliminating the build-up of coke deposits during a petrochemical process, comprising:

applying a slurry of the active coating of claim 32 to the metal surface of the reactor component, wherein the coating bonds thereto.

**43.** The method of claim 40, wherein the coating is applied by at least one of sponging, painting, centrifuging, spraying and by dipping/fill-up techniques.

**44.** The method of claim 40, wherein the coating is from about 25 to about 50 microns thick.

**45.** The method of claim 40, wherein the petrochemical process is a hydrocarbon cracking process.

**46.** The method of claim 40, wherein the reactor component is a component that is susceptible to coke formation thereon.

**47.** The method of claim 40, wherein the reactor component is selected from the group consisting of a furnace, a tube fitting, a reaction vessel, and a radiant tube.

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