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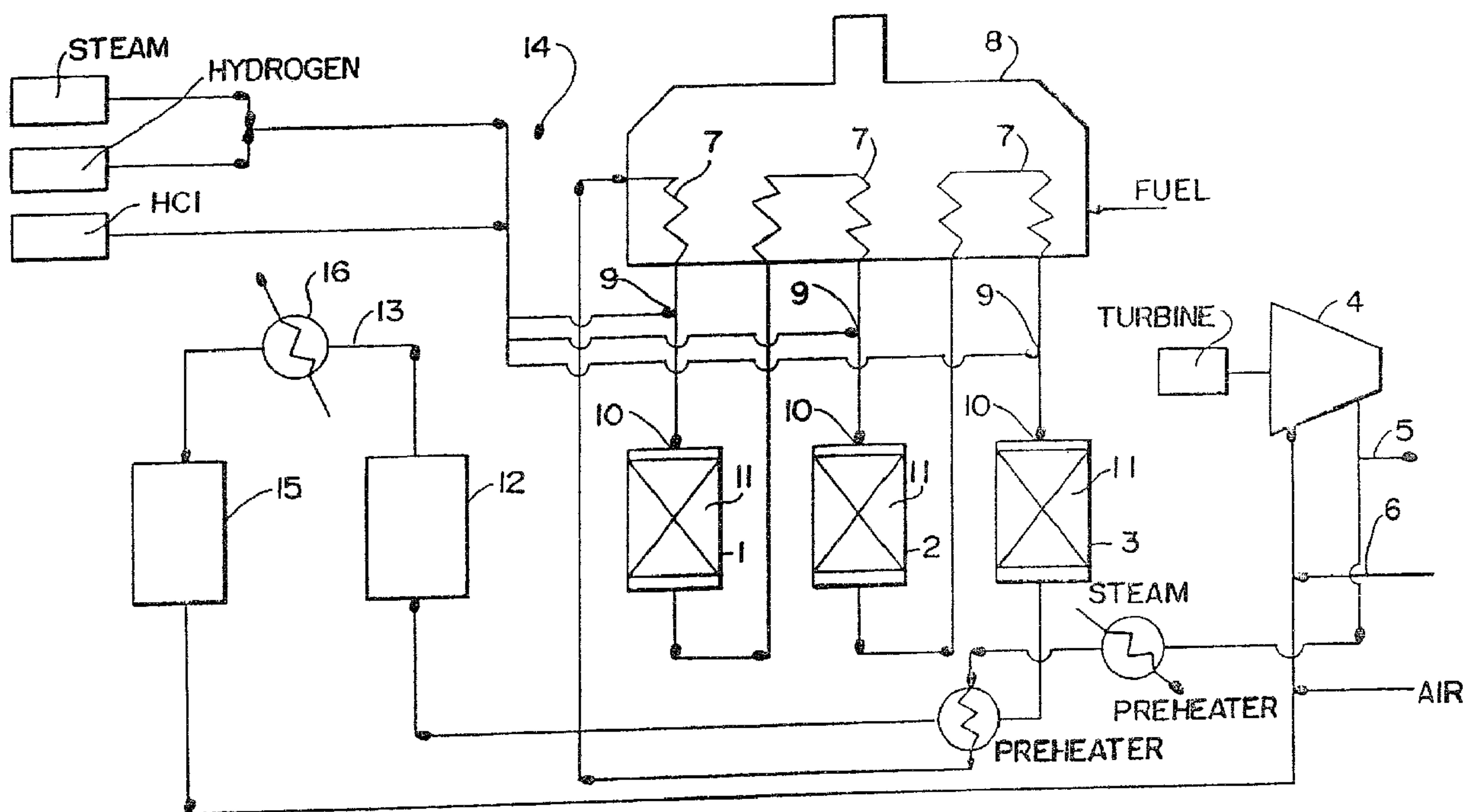
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(54) Titre : INSTALLATION ET METHODE POUR REGENERER DES CATALYSEURS A BASE DE ZEOLITE

(54) Title: APPARATUS AND METHOD FOR REGENERATING DEACTIVATED ZEOLITE REFORMING CATALYSTS



(57) Abrégé/Abstract:

The present invention is directed to an apparatus for treating a catalyst including facilities for removing at least one member selected from the group consisting of elemental mixtures of elemental halogen, halogen containing compounds and water from a gas stream to be passed through said catalyst during a treatment selected from the group consisting of regeneration of a deactivated catalyst and predispersion of catalytic metals in fresh catalysts. The present invention is also directed to apparatus for treating a catalyst which includes facilities for introducing substances selected from the group of substances required for regeneration of used catalyst and substances required for redispersion of catalytic metal of fresh catalyst into the inlet of each of the reactors. Related to this, the present invention is directed to a process for treating catalyst contained in a plurality of reactors which involves exposing a catalyst including at least one Group VIII metal contained in the reactors to oxygen and halogen so as to redisperse the metal, wherein the step of exposing involves initiating halogen flow to each of the reactors and adjusting the

(57) Abrégé(suite)/Abstract(continued):

halogen flows rate through the reactors so that halogen breakthrough from the reactors is substantially simultaneous. The present invention is also directed to a process for treating a zeolite-based catalyst contained in a plurality of reactors which involves exposing catalyst composed of catalytic metal selected from the group of Group VIII metals in an unreduced state contained in one of said reactors to a gas stream containing a reducing agent to substantially completely reduce the Group VIII metal, and maintaining catalyst composed of catalytic metal in an unreduced state contained in the other reactors in an atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water.



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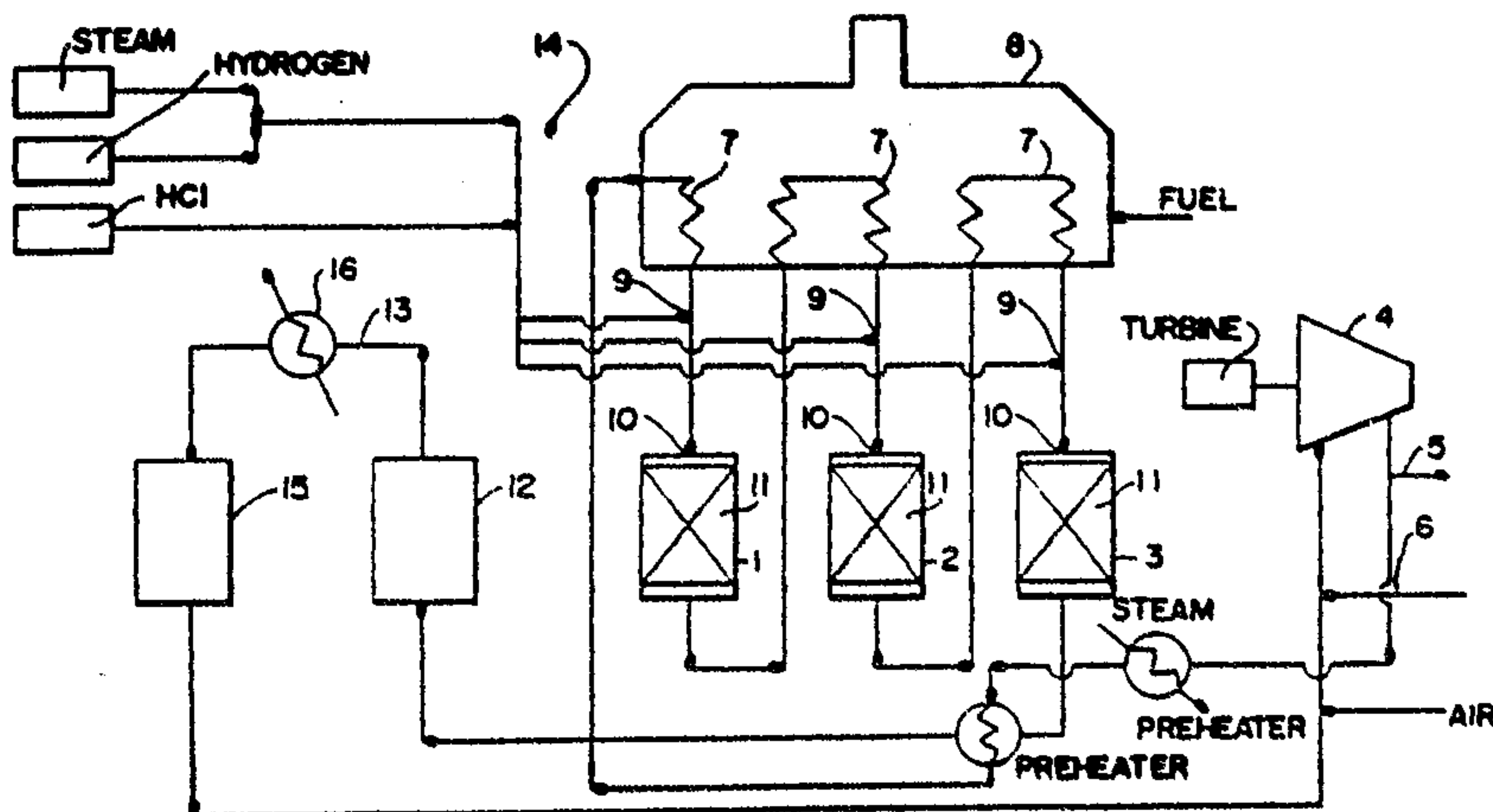
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(54) Title: APPARATUS AND METHOD FOR REGENERATING DEACTIVATED ZEOLITE REFORMING CATALYSTS

(57) Abstract

The present invention is directed to an apparatus for treating a catalyst including facilities for removing at least one member selected from the group consisting of elemental mixtures of elemental halogen, halogen containing compounds and water from a gas stream to be passed through said catalyst during a treatment selected from the group consisting of regeneration of a deactivated catalyst and predispersion of catalytic metals in fresh catalysts. The present invention is also directed to apparatus for treating a catalyst which includes facilities for introducing substances selected from the group of substances required for regeneration of used catalyst and substances required for redispersion of catalytic metal of fresh catalyst into the inlet of each of the reactors. Related to this, the present invention is directed to a process for treating catalyst contained in a plurality of reactors which involves exposing a catalyst including at least one Group VIII metal contained in the reactors to oxygen and halogen so as to redisperse the metal, wherein the step of exposing involves initiating halogen flow to each of the reactors and adjusting the halogen flow rate through the reactors so that halogen breakthrough from the reactors is substantially simultaneous. The present invention is also directed to a process for treating a zeolite-based catalyst contained in a plurality of reactors which involves exposing catalyst composed of catalytic metal selected from the group of Group VIII metals in an unreduced state contained in one of said reactors to a gas stream containing a reducing agent to substantially completely reduce the Group VIII metal, and maintaining catalyst composed of catalytic metal in an unreduced state contained in the other reactors in an atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water.



APPARATUS AND METHOD FOR REGENERATING DEACTIVATED
ZEOLITE REFORMING CATALYSTS
BACKGROUND OF THE INVENTION

5 1. Field of Invention

This present invention relates to regenerating deactivated catalysts. More particularly, the present invention is directed to apparatus and methods for regenerating deactivated reforming catalysts, containing one or more Group VIII metals. More specifically, the present invention is directed to apparatus and methods for regenerating reforming catalysts supported on zeolites and, in particular, to monofunctional, non-acidic reforming catalysts supported on large pore zeolites, and preferably zeolite L containing platinum.

15 2. Discussion of Background and Material Information

Catalytic reforming is a major petroleum refining process used to raise the octane rating of naphthas (C6 to C11 hydrocarbons) for gasoline blending. Catalytic reforming is also a principle source of aromatic chemicals, i.e., benzene, toluene and xylenes, via conversion of paraffins and naphthenes to aromatics.

20 The principle reforming chemical reactions are dehydrogenation of cyclohexane to aromatics, dehydrocyclization of paraffins to aromatics, dehydroisomerization of alkylcyclopentanes to aromatics, isomerization of normal paraffins to branched paraffins, dealkylation of alkylbenzenes, and hydrocracking of paraffins to light hydrocarbons. The hydrocracking of paraffins to light hydrocarbons is undesirable and should be minimized because light hydrocarbons have low value.

30 Reforming is typically carried out at temperatures of 800°F to 1000°F, pressures of 50 psi to 3000 psi, hourly weight

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space velocities of 0.5 to 3.0, and in the presence of hydrogen at molar ratios to feed of 1 to 10.

5 Conventional production line-scale reforming plants include a plurality, e.g. three or four, adiabatic packed bed reactors containing different amounts of catalyst connected in series, commonly referred to as a reactor train. In conventional reforming processes, the naphtha feed is vaporized, mixed with hydrogen, and preheated in a furnace to a temperature within the range of about 800°F to 1000°F and fed
10 into the inlet of the lead reactor. Inasmuch as reforming is a net endothermic process, the temperatures of reactor effluents are typically below or in the lower end of a reforming temperature range of 800°F to 1000°F, thus requiring that the reactor effluent streams be reheated in furnaces
15 installed upstream of each of the reactors.

The product stream from the last downstream reactor is cooled and flashed to low pressure in a drum and separated into a liquid reformat stream which is rich in aromatics and a gas stream which is rich in hydrogen. Part of the
20 hydrogen-rich stream is recycled into the feed stream to provide the hydrogen to feed ratio required for the process. Hydrogen is a by-product of reforming and the net hydrogen produced is removed as a gas stream from the flash drum and purified.

25 Catalysts currently used in commercial reformers include a Group VIII metal, such as platinum, or platinum plus a second catalytic metal, such as rhenium or iridium, dispersed on an alumina substrate. Typically, chlorine is incorporated on the alumina to add acid functionality. Alumina-based
30 reforming catalysts are suitable for aromatizing C₈ paraffins, but are less effective for aromatizing C₆ to C₈ paraffins because these catalysts hydrocrack more of the lighter paraffins to low value fuel gas than they convert to

aromatics.

Conventional commercial catalysts are bifunctional, i.e., the catalysts enhance i) dehydrogenation and cyclization reactions on the catalytic metal sites; and ii) isomerization on separate strong acid sites in the catalyst. The undesirable hydrocracking reactions also occur on the acid sites.

Within the past few years reforming catalysts have been developed which have been discovered to be particularly effective for aromatizing the C₆ to C₈ paraffin components of naphtha. These catalysts are made using zeolite, rather than alumina, as the support for the catalytic metal. They are mono-functional and contain relatively few strong acid sites. Unlike conventional bifunctional catalysts, zeolite based catalysts accomplish dehydrogenation and cyclization reactions as well as isomerization on the dispersed metallic catalytic sites. Because these zeolite-based catalysts have few strong acid sites, undesirable hydrocracking reactions are repressed.

Zeolites which are preferred for reforming catalysts are large pore zeolites i.e. zeolites with a 6 to 15 Angstrom pore diameter. Suitable large pore zeolites for purposes of the present invention include zeolite X, Y, and L, with zeolite L being the most preferred support for reforming catalysts, particularly wherein the catalytically active metal is platinum.

For production line-scale reforming processes, zeolite is preferably formed into aggregates, such as extrudates or tablets, typically 1/32 to 1/4 inches in size; otherwise if the reactor bed is packed with zeolite powder, the pressure drop across zeolite powder, packed reactor beds would be unacceptably high and powder losses via elutriation in reactor off-gas would be excessive. For forming the zeolite into aggregates, oxides, such as alumina or silica, may be used as binder materials.

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During reforming, catalysts deactivate due to accumulation of coke deposits in the catalyst, and agglomeration of the fine catalytic metal particles dispersed in the catalyst into larger particles. Therefore, it is common practice to periodically regenerate reforming catalysts to recover their activity. Unexpectedly, however, it was found that it is more difficult to regenerate the previously described zeolite-based reforming catalysts than the conventional alumina-based catalysts.

In general, such regeneration procedures include: 1) burning off the coke deposits using oxygen, and optionally a halogen or halogen containing compound, 2) redispersing the active catalytic metals by oxyhalogenation using , for example, HCl, oxygen and water, 3) stripping excess halogen off the catalyst using first wet air, and then dry air as a stripping gas, and 4) reducing the dispersed catalytic metal using a reducing agent such as hydrogen.

In attempts to overcome problems experienced during regeneration of large-pore, zeolite-based reforming catalysts, various procedures have been developed, for example as disclosed in U.S. Patent Nos. 4,552,856, 4,595,668, 4,595,669, 4,595,670, 4,634,517 and 4,648,960.

U.S. Patent 4,568,658, POEPPEIMEIER et al.; U.S. Patent 4,595,695, FUNG et al.; and U.S. Patent 4,595,670, TAUSTER et al., attempt to improve the reforming characteristics of zeolite-based catalysts by improving the dispersion of catalytic metals in fresh catalysts, i.e., catalysts which have not been "put on oil", and which do not contain coke products, to increase the initial activity and selectivity of the fresh catalysts relative to its performance on oil with no preemtioned dispersion.

U.S. Patent No. 3,986,982, CROWSON et al.; U.S. Patent No. 4,493,901, BERNARD et al.; U.S. Patent No. 4,645,751, McMullen et al.; U.S. Patent No. 4,851,380, Van LEIRSBURG et al.; U.S. Patent No. 4,855,269, MOHR and U.S. Patent No. 4,810,683, COHN et al. are directed to regeneration of zeolite-based catalysts.

U.S. Patent No. 3,986,982, CROWSON et al., discloses that oxidative burn-off to remove carbonaceous deposits should be performed in a manner which controls water produced from the hydrogen present in the deposits, or added, by drying the inert gas when the inert gas is recycled so as to effect a water content of the gas at the inlet which is below 200 ppm volume.

U.S. Patent No. 4,493,901, BERNARD et al., discloses that the selectivity of regenerative zeolite-based aromatization catalysts may be improved by adding a quantity of water up to about 10% by weight with respect to the catalyst to the air used to cool the catalyst after the oxychlorination step.

U.S. Patent No. 4,645,751, MCCULLEN et al., is directed to regeneration of deactivated noble metal containing zeolite catalysts which involves initially reducing the deactivated catalyst in hydrogen, pretreating the thus reduced catalyst with an inert gas stream containing about 0.001 to 10 weight percent hydrogen chloride, redispersing the noble metal with an inert gas stream containing about 0.001 to 10 weight percent Cl in the form of Cl₂ or Cl⁻ containing organic material, and subsequently reducing the catalyst. It is disclosed that the Cl treatments may optionally occur in the presence of oxygen or sources of oxygen.

U.S. Patent No. 4,851,380, VAN LEIRSBURG et al., is directed to a process for regenerating sulfur contaminated reforming catalysts composed of a zeolite and Group VIII metal which involves intentionally agglomerating the Group VIII

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metal into large agglomerates and then treating the catalyst with a halogen acid gas to remove sulfur contaminants.

U.S. Patent No. 4,855,269, MOHR, is directed to a process for regenerating contaminated monofunctional, large-pore zeolite catalysts formed and bound using an inorganic binder which involves (a) contacting the catalyst under oxychlorinating conditions with a gas comprising 1% to 21% oxygen, 1% to 4% water, and an effective amount of chlorine atoms to achieve a chlorine to platinum ratio between 4:1 and 1000:1; (b) contacting the catalyst with a gas comprising nitrogen, for a time between 150 and 1500 GHSV, and at a temperature between 850° and 950°F; and (c) contacting the catalyst with a gas comprising hydrogen having less than 1000 ppm water, at a temperature between 800°F and 950°F and a gas rate between 150 and 1500 GHSV.

U.S. Patent No. 4,810,683, COHN et al., discloses that the activity of non-acidic, zeolite-based Group VIII metal catalysts which have become deactivated, in part due to the deposition of carbonaceous materials, may be restored by subjecting the deactivated catalyst to a procedure which involves a first step of contacting the deactivated catalyst with a gaseous stream comprising oxygen, a halogen, or a halogen-containing compound or a mixture thereof, and an inert component at regeneration conditions including a temperature of from 350°C-600°C sufficient to combust at least a portion of said carbonaceous materials for a first period of time. This first step is followed by the second step of reducing the catalyst by contacting the catalyst with a gaseous stream comprising hydrogen at an elevated temperature for a period of time sufficient to produce a reduced/regenerated hydrocarbon conversion catalyst.

In addition to these patents, procedures are known

for improving the activity and selectivity of deactivated type L zeolite-based catalysts by dispersing the catalytic metal throughout the pores or channels of the zeolite. Various procedures for dispersing the catalyst metal on the zeolite L substrate are also known.

U.S. Patent No. 4,914,068 filed March 21, 1988, in the name of FUNG et. al.,
5 entitled "Process for the Dispersion of Group VIII metal in Large Pore Zeolite Catalysts", discloses the advantages of a reduction step practiced at a temperature sufficiently lower than the chlorination or oxychlorination step and the benefits of cooling the catalyst in the presence of oxygen before the reduction.

U.S. Patent 4,595,669, commonly owned with the present application, which
10 issued from U.S.S.N. 550,902 filed on November 10, 1983 in the name of Shun C. Fung and Samuel Tauster is directed to a process for improving the dispersion of noble metals by an oxychlorination procedure.

Oxychlorination, i.e., dispersion of the noble metal, may be accomplished by exposing the catalyst at temperatures within the range of 400°C to 530°C for up to ten
15 hours to a gas stream containing 0% to 10% by volume of water; elemental chlorine with or without oxygen; hydrogen chloride and oxygen; chlorinated hydrocarbons, such as carbon tetra-chloride; and oxygen.

It was discovered, however, that the apparatus and methods in accordance with the present invention were required

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in order to make such regeneration procedures operable in production line-scale plants.

5 The apparatus and methods in accordance with the present invention are solutions to unexpected problems encountered when regeneration procedures were scaled up from laboratory test equipment to production size plants.

10 In the laboratory, the inert gas, such as nitrogen, is normally passed once through the catalyst and then discarded. In a large-scale plant, however, once-through gas flow is impractical. Carrier gas is recycled with a fraction of the recirculating gas purged and replaced with fresh make-up inert gas. During regeneration, HCl is expelled from the catalyst into the recirculating inert carrier gas and when the inert carrier gas is recycled, HCl concentration builds up to
15 relatively high levels in the recirculating carrier gas; and high levels of HCl in the carrier gas stream have been found to adversely affect redispersion of the catalytic metals. Accordingly, an HCl trap is installed in the recycled gas line to remove HCl from recycling carrier gas.

20 Also, during regeneration, a change is made from wet carrier gas to dry carrier gas, and it has been discovered that when carrier gas is recycled, it takes an unacceptably long time to reduce the water content in the carrier gas, which impedes the regeneration of zeolite reforming catalysts.
25 Accordingly, a water trap is installed in the recycled gas line to remove water from recycling carrier gas.

30 In laboratory units, reactors are regenerated one at a time and gas space velocity is high, e.g., WHSV of 4-10 reciprocal hours. In large scale plants, several reactors are connected in series, and space velocities during regeneration are low, e.g., WHSV of 1.0-1.5 reciprocal hours. As a result, the time to complete the oxychlorination, as evidenced by the appearance of chlorine in the reactor effluent gas, in large

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scale plants, is excessively long if chlorine is added only to the inlet of the upstream reactor. This exposes catalyst in the upstream reactors to oxychlorination conditions for excessively long times which impairs performance of regenerated catalyst. Accordingly, facilities and procedures are employed to add chlorine to the inlet of each reactor and to achieve complete chlorination of catalyst in all reactors, as evidenced by appearance of chlorine in the reactor outlet gas, at about the same time.

10 The apparatus of the present invention includes: facilities for feeding, measuring and controlling substances required to regenerate catalyst separately to the inlet to each reactor; facilities for removing halogen and halogen compounds from the feed to the lead reactor in the reactor train; and facilities for removing water from the feed to the lead reactor in the reactor train.

15 The procedures associated with the apparatus include: (1) treating the catalyst in each reactor with a gas stream comprising halogen, oxygen, and an inert gas, and fixing the time of halogen initiation and halogen flow rate to each reactor in the train such that halogen breakthrough occurs substantially simultaneously from all reactors; (2) reducing the catalytic metals in the catalyst with a reducing agent so as to preclude exposing catalyst to halogen prior to reduction. This is accomplished by reducing the reactors one at a time moving from tail reactor to lead reactor and using the halogen removal facility to remove halogen from gas recycled from the tail reactor outlet to the lead reactor inlet; and (3) reducing the time required to switch from wet to dry conditions when recycling treat gas by removing water from the treat gas using the water removal facility.

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SUMMARY OF INVENTION

5 It has been discovered that certain apparatus and procedure improvements are required to successfully apply regeneration procedures for zeolite based reforming catalysts to large-scale production plants. These improvements are the subject of this invention.

10 Reforming catalysts, zeolite catalysts included, deactivate in normal operation due to deposition of coke and agglomeration of dispersed catalytic metals into large particles. Deactivation is progressive. In an attempt to compensate for deactivation of the catalyst, the temperatures of the reactor inlet streams are raised. Eventually, however, maximum temperature limits are approached and the catalyst must be regenerated.

15 Regeneration of zeolite catalysts includes four basic operations:

- i) removal of coke, typically by burning;
- ii) redispersion of the agglomerated metal, typically by oxychlorination;
- 20 iii) stripping chlorine off the catalyst using wet and dry air; and
- iv) reduction of metal chloride to the metal state using a reducing agent, such as hydrogen.

25 As previously stated, in production scale plants inert carrier gas is recycled to conserve carrier gas. During hydrogen reduction and stripping, HCl is released into the recirculating inert carrier gas and builds up rapidly to high concentration which, it has been discovered, interferes with effective redispersion of the catalytic metals.

30 In accordance with the present invention, an HCl trap may be included in the recycle gas line between the lead and tail reactors to limit HCl concentration build-up in the recycle gas. The HCl trap removes HCl from the recirculating carrier

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gas and prevents HCl concentration from building up in the gas stream. The preferred HCl trap is sodium hydroxide on promoted alumina. Katalco's™ 59-3 is a particularly suitable commercially available sodium hydroxide on promoted alumina
5 which has been successfully employed.

Further, the regeneration procedure requires changing from wet to dry carrier gas during stripping. In large-scale plants, the time required to dry the recycling inert gas stream exceeds prescribed desirable limits so that catalyst
10 regeneration and performance is impaired. In accordance with the present invention, therefore, a water trap is included in the gas recycle loop between the lead and tail reactors to reduce the time required to dry the recycling gas stream. The water trap is also useful for removing water emitted by the
15 catalyst during reduction which, if allowed to build up in the recycling inert gas, would impair catalyst performance. Although the water trap can be any suitable drying material, a 4A mol sieve is particularly preferred.

Another aspect of the present invention arises because
20 the multiplicity of the reactors in the commercial reactor train are connected in series during regeneration, with inert carrier gas flowing sequentially through them. As a practical matter, it is difficult to isolate the reactors so they can be regenerated one at a time. As a result, carrier gas
25 space velocities (ratio of carrier gas flow rate to catalyst volume) are lower in production large-scale plant reactor systems than in laboratory systems.

This causes overchlorination of catalyst in upstream reactors which is deleterious to catalyst performance. The
30 catalyst absorbs chlorine and hydrogen chloride from the carrier gas until the catalyst is saturated with chlorine. The chlorine and hydrogen chloride breakthrough wave moves steadily downstream from the inlet to the lead reactor to the

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outlet of the tail reactor at a rate directly proportional to the chlorine gas feed rate. Accordingly, in production-scale plants, catalyst in the upstream reactors can be exposed to chlorine and hydrogen chloride for time periods and at concentrations which exceed prescribed desirable limits although these limits are easily satisfied in lab units by isolating the reactors and regenerating them one at a time. This subjects upstream catalyst in production-scale plants to extended exposure to chlorination gases after the catalyst has been oxychlorinated and the chlorine breakthrough wave has moved downstream. Overchlorination impairs regeneration and subsequent performance of the catalyst. Accordingly, an aspect of this invention is to conduct the oxychlorination step to achieve substantially simultaneous halogen breakthrough from all of the reactors.

Therefore, in accordance with the present invention, in order to limit overchlorination of upstream catalyst, apparatus for introducing, metering, and controlling flow of halogen and water into the inlet of each reactor are provided. These facilities are used to initiate oxychlorination redispersion to each reactor separately at different times and at different chlorine feed rates rather than initiating flow of chlorine only to the lead reactor and the downstream reactors. Flow of hydrogen chloride and water to a reactor is started sooner and/or at higher halogen feed rate in proportion to the quantity of catalyst contained in the reactor such that chlorine breakthrough in the effluent from each reactor occurs at about the same time for all reactors even though the reactors contain different amounts of catalyst. This minimizes deleterious exposure of upstream catalyst to chlorination gases after the catalyst has been oxychlorinated and the chlorine breakthrough wave has moved downstream.

Further, it has been discovered that exposing catalyst to HCl after the catalytic metal has been dispersed and reduced is innocuous. In contrast, exposing the catalyst to HCl before the catalyst metal is reduced impairs regeneration and subsequent performance of the catalyst. As previously described, HCl is released from the catalyst into the recycling carrier gas during reduction of the catalytic metal with hydrogen. Build-up of HCl concentration in the recirculating carrier gas stream is mitigated by using an HCl trap in the recycle carrier gas line between the tail and lead reactors. In addition, it has been discovered that it is beneficial to reduce the reactors one at a time in a certain preferred sequence. Therefore, in accordance with the present invention, facilities are provided for initiating flow of hydrogen into all reactors independently. The flow of H₂ gas is initiated first into the tail reactor and the HCl trap is employed to prevent HCl released in the tail reactor from being carried into the lead reactor by the recirculating carrier gas.

After the catalyst in the tail reactor has been completely reduced as evidenced by termination of HCl evolution, reduction of catalyst in the reactor immediately upstream of the tail reactor is initiated by starting hydrogen flow into that reactor. HCl is released and is carried into the tail reactor in the carrier gas but it does no harm because catalyst in the tail reactor has already been reduced. Again preferably an HCl trap is employed to remove HCl from the recycling carrier gas to prevent HCl from being carried into the lead reactor, which has not yet been reduced. This operation is again repeated for the next upstream reactors until the lead reactor is reduced.

Further, during reduction, when hydrogen flow to a reactor is initiated, in addition to evolving HCl, the

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catalyst also releases water into the recirculating carrier gas. The aforementioned water trap in the recycle gas line may be used to prevent build-up of water concentration in the recirculating carrier gas to deleteriously high levels.

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BRIEF DESCRIPTION OF THE DRAWINGS

The Figure is a flow diagram of the process employing the apparatus in accordance with the present invention.

DETAILED DESCRIPTION

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The present invention is directed to an apparatus for the regeneration of a deactivated catalyst and redispersion of catalytic metals in fresh catalysts, wherein the apparatus includes means for separation of at least one member selected from the group consisting of elemental halogen, halogen containing compounds, water and mixtures of elemental halogen, halogen-containing compounds, and water from a gas stream to be passed through a catalyst during a treatment selected from the group consisting of regeneration of a deactivated catalyst and predispersion of catalytic metals in fresh catalysts. The means for separation includes means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds from the gas stream and/or means for removing water from the gas stream. In the latter instance the means for removing water may be selected from the group consisting of a water trap and a fixed bed drier. In the embodiment where the means for removing water is a fixed bed drier, the fixed bed drier comprises a mol sieve, which is preferably selected from the group consisting of a 4A mol sieve and a 5A mol sieve. In the embodiment where the means for separation includes means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds from the gas stream, such means may be selected from the group consisting of a fixed bed adsorber, a water scrubber, and a

caustic scrubber, wherein the fixed bed adsorber comprises sodium hydroxide on promoted alumina, and the caustic scrubber comprises means for contacting the gas with caustic solution and means for removing caustic solution containing halogen from the gas stream.

In one embodiment, the means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds and the means for removing water may be connected in series in a line for supplying the gas stream to the catalyst, in which case the means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds is located upstream of the means for removing water from the gas stream in the line. The apparatus may also include means for reducing the temperature of the gas stream located upstream of the means for removing water in the line, preferably wherein the means for reducing the temperature of the gas stream is located downstream of the means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds in the line.

The apparatus in accordance with the present invention may also include a compressor with its suction inlet located downstream from the means for removing water in the line, in addition to means for supplying at least one fluid to the line communicating between a source of the at least one fluid and the line, and means for releasing fluid from the line communicating between the line and the ambient, which is preferably a purge line located downstream from the compressor.

For purposes of the present invention, as used herein, the at least one fluid may be at least one member selected from the group consisting of steam, hydrogen, a hydrogen halide, a source of halogen, air and an inert gas. In one

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instance, the fluid is a substance or substances required for regeneration of used catalysts and substances required for predispersion of catalytic metal in fresh catalyst selected from the group consisting of steam, hydrogen, and a source of halogen, in which case the means for supplying the at least one fluid is located downstream from the compressor and upstream of the reactor inlets; in another instance, the fluid may be a gas selected from the group consisting of air, oxygen, and an inert gas, wherein the means for supplying is located between the means for removing water from the gas stream and the compressor. Preferably, the inert gas is nitrogen.

In a preferred embodiment, the apparatus in accordance with the present invention includes at least one reactor containing catalyst, and means for introducing substances selected from a group of substances required for regeneration of used catalyst and substances required for predispersion of catalytic metal in fresh catalyst into the reactor, preferably wherein the at least one reactor are a plurality of reactors including a lead reactor and a tail reactor, wherein the lead reactor includes an inlet and the means for introducing the substances is operably connected to add the substances to the reactor through the inlet. Preferably the apparatus in accordance with the present invention includes at least three reactors, wherein the supply of the substances is operably connected to the means for introducing at least one member selected from the group consisting of a source of water, a source of reducing agent, and a source of halogen, preferably wherein the supply of the substances includes a source of steam, a source of hydrogen, as well as a source of HCl. In accordance with the present invention, each of the plurality of reactors includes an inlet, and each of the means for introducing is operably connected to add such substances

through the inlet of each of the plurality of reactors. Preferably, the apparatus in accordance with the present invention comprises at least one member selected from the group consisting of means for controlling, means for metering, and means for measuring concentrations of the substances operably connected to the means for introducing.

The catalyst treated in accordance with the present invention preferably comprises a zeolite and at least one Group VIII metal, wherein the zeolite is a large pore zeolite, preferably having a pH within the range of about 9.4 to 10.0. Preferably, at least 30% of the large pore zeolite is zeolite L, wherein at least 50% of said zeolite L are crystallites with circular cylinders having an aspect ratio of at least 0.5, and a mean diameter of at least 0.2 microns.

Most preferably, the large pore zeolite comprises exchangeable cations, which are preferably selected from the group consisting of potassium, sodium, strontium, barium, calcium, lithium, magnesium, rubidium, cesium and copper, and mixtures of two or more members selected from the group consisting of potassium, sodium, strontium, barium, calcium, lithium, magnesium, rubidium, cesium and copper. The most preferred Group VIII metal is platinum, and the more preferred exchangeable cations in said zeolite are potassium and barium with potassium being the most preferred. Preferably, the zeolite is in the form of aggregated particles, wherein said aggregated particles are selected from the group consisting of extrudates, tablets, and spheres. Preferably, the aggregated particles comprise a binding material selected from the group consisting of metal oxide and clays. More preferably, the binder material is a member selected from the group consisting of alumina, silica and alumina-silicates. In general, however, the catalyst treated in accordance with the present invention may be non-acidic and monofunctional.

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The present invention is also directed to a process for treating catalyst contained in a plurality of reactors which involves exposing a catalyst including at least one Group VIII metal contained in the reactors and adjusting the halogen flow rate through the reactors so that halogen breakthrough from the reactor occurs substantially simultaneously from all reactors. One can compute time of exposure to halogen to halogen breakthrough according to the formula:

$$T = (W/R) K$$

where W is the weight of the catalyst in a reactor, R is the rate of halogen flow to that reactor, T is the time of exposure to halogen to halogen breakthrough, and K is a constant that is characteristic of the catalyst and the units selected to express weight, time and volume. Halogen flow is initiated first to the reactor requiring the longest halogen exposure time, second to the reactor requiring the next longest halogen exposure time and moving in this fashion until halogen flow is initiated last into the reactor requiring the shortest halogen exposure time. Initiation times are staggered so that the difference in initiation times equals the difference in required halogen exposure time. Following this procedure halogen breakthrough will occur at about the same time from all reactors. This minimizes needless exposure of catalyst to halogen.

Typically, process plants have at least three reactors, wherein one of the reactors contains the heaviest weight of catalyst and another of said reactors contains the lightest weight of catalyst, and the process involves introducing halogen flow first to the reactor contains the heaviest weight of catalyst and last to another of the reactors containing the lightest weight of the catalyst. In a preferred embodiment, where the at least three reactors include a lead reactor and a tail reactor, wherein one of the reactors containing the

heaviest weight of catalyst is the tail reactor, and wherein another of the reactors containing the lightest weight of catalyst is the lead reactor, the halogen flow is introduced first to the tail reactor, and last to the lead reactor.

5 For purposes of the present invention, the halogen is selected from the group consisting of sources of chlorine, which are selected from the group consisting of Cl_2 , HCl , and chlorinated hydrocarbons, preferably selected from the group consisting of chloroform, methyl chloride, carbon
10 tetrachloride, 1,2- dichloroethane, trichloroethane, and mixture of one or more members selected from the group consisting of Cl_2 , HCl , chloroform, methyl chloride, carbon tetrachloride, 1,2- dichloroethane and trichloroethane, preferably wherein the source of chlorine is HCl .

15 The present invention is also directed to a process for treating a zeolite-based catalyst including at least one Group VIII metal contained in a plurality of reactors including a lead reactor and a tail reactor which involves exposing catalyst including catalytic metal selected from the group of
20 Group VIII metals in an unreduced state contained in one of the reactors to a gas stream containing a reducing agent to substantially completely reduce the Group VIII metal; and maintaining catalyst including the catalytic metal in an unreduced state contained in the other reactors in an
25 atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water. Preferably the process in accordance with this embodiment of the present invention also involves introducing a gas stream containing a reducing agent into another of the reactors
30 containing catalyst including the catalytic metal in an unreduced state and exposing the catalytic metal to substantially completely reduce the catalytic metal while maintaining catalyst including the catalytic metal in an

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atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water until the catalyst including the catalytic metal in each of said reactors is substantially completely reduced whereby the catalyst metal is only exposed to a halogen subsequent to being reduced. Typically, the plurality of reactors include a lead reactor and a tail reactor and wherein the step of exposing involves introducing a gas stream which is substantially devoid of at least one member selected from the group consisting of halogen, halogen-containing compounds, and water to the tail reactor; passing the gas stream through the tail reactor; subsequently introducing the gas stream to the lead reactor; and passing the gas stream through the lead reactor until the catalytic metal of said catalyst contained in the lead reactor is substantially completely reduced.

More typically, the plurality of reactors are a series of reactors including at least one intermediate reactor positioned between the lead reactor and the tail reactor and the step of introducing the gas stream to each reactor is performed sequentially first through the tail reactor until reduction of the catalytic metal of the catalyst contained in the tail reactor is substantially complete; next introducing and passing the gas stream through each intermediate reactor until reduction of said catalytic metal of the catalyst contained in each intermediate reactor is sequentially, substantially completed; and finally introducing and passing the gas stream through the lead reactor until reduction of the catalytic metal of the catalyst contained in the tail reactor is substantially complete.

In addition, a gas stream including HCl and water is discharged from the tail reactor and a gas stream substantially devoid of HCl and water is introduced to the lead reactor, preferably wherein the HCl and H₂O is removed

from the discharged gas stream before the gas stream substantially devoid of HCl and water is reintroduced into the lead reactor.

5 Preferably, water is removed from the discharged gas stream, more preferably by passing the gas stream through means for removing water, which is a water trap, such as a mol sieve selected from the group consisting of a 4A mol sieve and 5A mol sieve, so as to result in a substantially dry gas stream substantially devoid of HCl wherein the step of
10 exposing involves introducing the substantially dry gas stream into the lead reactor. The step of removing HCl involves passing the discharged gas stream through means for removing HCl from the gas discharge stream to result in a gas stream substantially devoid of HCl, wherein the means for removing
15 HCl is an HCl trap. More preferably the process also involves removing water from the discharged gas stream substantially devoid of HCl, wherein the step of removing water involves passing the discharged gas stream substantially devoid of HCl through means for separating water from the discharged gas
20 stream, such as a water trap, which is preferably a mol sieve, preferably selected from the group consisting of a 4A mol sieve and a 5A mol sieve.

A preferred embodiment of the process of this invention includes reducing the temperature of the gas stream
25 substantially devoid of HCl to result in a cooled gas stream prior to passing the cooled gas stream through the means for separating water from the gas stream.

The most preferred embodiment of the present invention is directed to a process for treating zeolite and at least one
30 Group VIII metal contained in at least two reactors including a lead reactor and a tail reactor, in which the hydrogen reduction step includes: (a) reducing the dispersion of the at least one Group VIII metal in said catalyst; (b)

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recirculating a carrier gas stream discharged from one of the reactors to an inlet of another of the reactors; and (c) removing at least one member selected from the group consisting of HCl, water and mixtures of HCl and water from the discharged gas stream before reintroducing the gas stream into said inlet.

Preferably the discharged gas stream is cooled to a temperature below the dew point of said gas stream. The process also preferably involves removing water from the cooled gas stream, so as to result in a substantially dry carrier gas stream and then introducing the substantially dry gas stream into said lead reactor.

In this embodiment, the process preferably also involves exposing the catalyst in an unreduced state contained in one of said reactors to a gas stream containing a reducing agent to substantially completely reduce the Group VIII metal; and maintaining the catalyst including catalytic metal in an unreduced state contained in the other reactors in an atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water, and introducing a gas stream containing a reducing agent into the next upstream reactor containing catalyst in an unreduced state and exposing the catalytic metal to the gas stream to substantially completely reduce catalytic metal while maintaining unreduced catalyst in an atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water until the catalyst in each of the reactors is substantially completely reduced whereby the catalyst metal is only exposed to a halogen subsequent to being reduced. The plurality of reactors include a lead reactor and a tail reactor and the step of exposing the catalyst to the gas stream involves introducing a gas stream which is substantially devoid of at least one member selected

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from the group consisting of halogen and water to the tail reactor; passing the gas stream through the tail reactor; subsequently introducing the gas stream to the lead reactor; and passing the gas stream through the lead reactor until said catalytic metal of said catalyst contained in said lead reactor is substantially completely reduced. Preferably the plurality of reactor are a series of reactors including at least one intermediate reactor positioned between the lead reactor and the tail reactor and the step of introducing the gas stream to each reactor is performed sequentially first through the tail reactor until reduction of the catalytic metal of the catalyst contained in the tail reactor is substantially complete; next introducing and passing the gas stream through each intermediate reactor until reduction of the catalytic metal of the catalyst contained in each intermediate reactor is sequentially, substantially completed; and finally introducing and passing the gas stream through the lead reactor until reduction of the catalytic metal of the catalyst contained in the tail reactor is substantially complete. The process of this embodiment of the present invention further involves discharging a gas stream including HCl and water from the tail reactor and introducing a gas stream substantially devoid of HCl and water to the lead reactor, wherein the HCl and H₂O is removed from the discharged gas stream before reintroducing the gas stream substantially devoid of HCl and water into the lead reactor.

The process in accordance with the present invention also involves exposing deactivated catalyst contained in the reactors to oxygen and halogen in order to redisperse metal and result in substantially simultaneous halogen breakthrough for all of said reactors, preferably by initiating halogen flow at a flow rate to each of said reactors and adjusting the halogen flow rate through said reactors so that halogen

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breakthrough is substantially simultaneous from each of said reactors notwithstanding that at least two of the plurality of reactors contain a different amount of catalyst.

5 The Figure is a flow chart showing a catalytic reformer in regeneration alignment in accordance with the present invention. The following discussion explains how the apparatus and procedures in accordance with the present invention are used to improve regeneration of large pore zeolite based reforming catalysts and to contrast the
10 improvements with conventional reformer regeneration apparatus and procedures.

Referring to the figure, inert carrier gas, typically nitrogen, is recirculated through the reactors 1, 2, 3 piped in series using the recycle gas compressor 4. A fraction
15 (typically 10%) of the recirculating carrier gas is continuously purged through purge line 5 to prevent build-up of impurities in the recycling carrier gas, and fresh (make-up) nitrogen is added through line 6 to maintain required system pressure. Specified reactor inlet temperatures are
20 maintained using the feed effluent heat exchangers 7 and furnaces 8. In a conventional reformer the chemicals used to regenerate the catalyst, i.e., water (e.g., as steam), halogen, and hydrogen, are introduced at only one point in the circulating carrier gas loop, typically, just upstream of
25 the recycle gas compressor. However, the apparatus improvements of this invention include means for feeding, metering and controlling steam, reducing agent (hydrogen), source of halogen (preferably HCl), to the inlets 10 of each of the reactors in the train. These separate means for
30 feeding, metering and controlling such substances are particularly useful in the oxyhalogenation step of the regeneration procedure. If conventional procedures were used without the improvements of the present invention, i.e.,

wherein halogen were added only to the lead reactor, the time to halogen breakthrough at the outlet of the tail reactor could be 12 to 24 hours, and the catalyst near the inlet to the lead reactor would be exposed to halogen for 12 to 24 hours after passage of the chlorine breakthrough wave whereas the preferred exposure limit achieved in accordance with the present invention is about one to about two hours.

In accordance with the present invention, therefore, halogen and water are fed to the inlet of all reactors 1,2,3 in the train. The halogen flow rate to each reactor and time of initiation of halogen flow are selected, as described in more detail hereinbelow so that chlorine breakthrough from all reactors occurs at about the same time and oxychlorination time through the reactor with the most catalyst charge does not exceed about six hours.

Oxychlorination time can readily be computed using the equation:

$$T = (W/R)K$$

where W is the weight of catalyst in the reactor, R is the weight rate of halogen addition, T is the oxychlorination time to breakthrough, and K is a constant that is characteristic of the catalyst and the units selected to express weight and time, such that halogen flow is initiated first to the reactor requiring the longest halogen exposure time, second to the reactor requiring the second longest exposure time and continuing in this fashion until halogen flow is initiated last to the reactor requiring the shortest halogen exposure time and staggering the time separations between initiations of halogen wherein the initiation time delays are equal to the differences between estimated halogen exposure times so that the required halogen exposure time to breakthrough is completed simultaneously for all reactors.

Accordingly, the flow of halogen is initiated first to

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the reactor requiring the longest oxychlorination time. This is usually the reactor containing the most catalyst 11, which is shown in the Figure as reactor 3. Flow of halogen is next initiated to the reactor requiring the next longest oxychlorination time after a time delay from halogen initiation to the first reactor equal to the time increment or difference between the oxychlorination required for the first reactor and the oxychlorination time required for the second reactor. This procedure is repeated for the other reactor in the train. With this procedure halogen breakthrough will occur simultaneously from all reactor and exposure of oxychlorinated catalyst to halogen will be minimized.

Recirculation of carrier gas containing halogen is continued for one to five hours after halogen breakthrough to ensure that all the catalyst is thoroughly oxyhalogenated.

The apparatus in accordance with the present invention also includes a halogen trap 12 in the carrier gas recycle line 13 between the tail reactor 3 and lead reactor 1 and means or devices 14, for feeding, metering and controlling flow of reducing agent (typically hydrogen) to each reactor as shown in the Figure. The halogen trap 12 can be any material capable of quantitative absorption of the halogen released from the catalyst when the catalyst is reduced. One appropriate halogen trap is sodium hydroxide on an alumina extrudate such as Katalco's 59-3. The halogen trap is used during the reduction step. In conventional reformer systems which do not have a halogen trap, halogen concentration tends to build up rapidly in the recycling carrier gas when the reducing agent is fed into the carrier gas, and the catalyst is exposed to high concentrations of halogen before and during reduction which impairs regeneration and subsequent catalyst performance. In accordance with this invention, flow of reducing agent is started first to the tail reactor. In the

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case where the redispersion agent is chlorine and the reducing agent is hydrogen, HCl is evolved from the catalyst into the carrier gas. The HCl is adsorbed by the halogen trap which precludes build-up of HCl concentration in the recirculating carrier gas and shields the upstream reactors from exposure to HCl while they are still in a vulnerable unreduced state.

When reduction of the catalyst in the tail reactor is complete as evidenced by termination of HCl evolution, flow of reducing agent to the reactor next upstream to the tail reactor is started. This process is repeated until the lead reactor is reduced.

The apparatus in accordance with the present invention also includes a water trap 15 in the recycle carrier gas line between the tail and lead reactors as shown in the Figure. A cooler heat exchanger 16 is included upstream of the water trap to cool the carrier gas which increases the water retention capacity of the water trap. The water trap can be any material capable of quantitatively absorbing water out of the carrier gas stream. A preferred water trap is 4A mol sieve. Typically, the water trap is periodically regenerated by drying the trap bed with hot dry inert gas. In accordance with the present invention, the water trap is used to good advantage during the transition between wet and dry air soak.

The prescribed transition time is three to four hours which is achieved using the water trap; without the water trap it could take substantially longer to dry the system in making the wet to dry transition and the excessively long wet air soak would impair regeneration and subsequent catalyst performance.

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Large Pore Zeolite Reforming Catalysts

The present invention is directed to procedures and apparatus which have been discovered to be particularly preferred for regenerating large-pore zeolite catalysts. The catalysts for which the discoveries of the present invention are particularly suitable include large-pore zeolites, at least one Group VIII metal, and one or more cations from Group IA or IIA. As used herein, large pore zeolites are defined as zeolites having an effective pore diameter of between 6 and 15 Angstroms. The most preferred catalyst used in accordance with the present invention and which has been determined to perform exceptionally well as a light naphtha reforming catalyst substrate is a form of potassium zeolite L. It should be understood, however, that although the present invention may be described herein and examples given for performing the process and using the apparatus of the regeneration system in accordance with the present invention with respect to potassium zeolite L, such discussions and examples are presented as being illustrative of the preferred embodiment, and are not meant to limit the present invention which is appropriate for the regeneration of zeolite based reforming catalysts and preferably large pore zeolite catalysts.

Zeolite L, its x-ray diffraction pattern, and its properties, as well as its preparation are described in detail in U.S. Patent No. 3,216,789.

A composition of type L-zeolite expressed as mole ratios of oxides may be represented as follows:



wherein M designates a cation, n represents the valence of M and y may be any value from 0 to 9. The chemical formula can vary without changing the crystalline structure which is the

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distinguishing feature of zeolite L. For example, the silicon to aluminum ratio may vary from 1.5 to 3.5.

5 The catalyst performance of a zeolite L reforming catalyst depends on the morphology, i.e., the shape, form and regularity of the zeolite crystals. The preferred form of zeolite is described in U.S. Patent No. 4,544,539 and procedures to synthesize it are described in U.S. Patent No. 4,701,315.

10 The preferred form of zeolite L is distinguished from other zeolite L in that at least 50% of the zeolite crystallites are circular cylinders with an aspect ratio of at least 0.5 and mean diameter of at least 0.5 microns.

15 Zeolites normally contain exchangeable cations and zeolite L is usually synthesized in the potassium form. However, other cations can be incorporated into the zeolite by ion exchange with potassium, by impregnation, or by synthesis. Cations other than potassium that make useful catalysts are alkali metals selected from Group 1A and are
20 preferably selected from the group consisting of sodium, lithium, rubidium and cesium, and alkaline earth metals selected from Group IIA and preferably members selected from the group consisting of barium, calcium and strontium. A member selected from the group consisting of magnesium and
25 barium is more preferred. The most preferred exchangeable cation is potassium.

To be useful in production line-scale reactors, the catalysts should be formed into aggregates, such as pellets, tablets, extrudates, or spheres having a dimension within the
30 range of about 1/32 to 1/16 of an inch size for use in production line-scale packed bed reactors using conventional catalyst forming technology, for example as disclosed in U.S. Patent Nos. 3,326,818; 3,557,024; 4,046,713; 4,458,025;

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4,517,306; and 4,447,316.

The aggregates may be formed using 10% to 85% inorganic oxides on zeolite as a matrix to bind the zeolite. Suitable binders include alumina, silica, alumina-silicates and clays. It is preferred to extrude catalysts using alumina as the binder matrix.

The catalysts must also contain one or more Group VIII metals well dispersed in the zeolite. Suitable metals include members selected from the group consisting of platinum, iridium, palladium and rhenium. The metal most preferred is platinum. The percentage of platinum in the most preferred catalyst is in the range of 0.1 to 2% by weight of the catalyst.

The Group VIII metals can be introduced into the zeolite after forming the zeolite into an aggregate, or into zeolite before forming into an aggregate, by either impregnation or ion exchange. Also, procedures are available for incorporating catalytic metals into the zeolite during synthesis of the zeolite. For impregnation, the platinum source can be aqueous solutions comprising a member selected from the group consisting of tetraamineplatinum (II) nitrate, tetraamineplatinum (II) chloride, and dinitrodiamino-platinum (II). For ion exchange a cationic platinum complex, such as tetraamineplatinum (II) nitrate is suitable. It is preferred, however, to load the catalytic metal into the aggregate or extrudate using a procedure in which both the final pH and excess potassium of the extrudate is controlled as it is withdrawn from the loading vessel. A preferred metal loading procedure is described in detail in U.S. Patent No. 4,568,656.

It has been determined that zeolite catalysts in which

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the Group VIII metals are dispersed such that at least 90% of the metal particles have diameters less than 7 Angstroms are superior reforming catalysts and are, therefore, preferred. The catalysts preferred for purposes of the present invention
5 are described in U.S. Patents Nos. 4,595,668, 4,595,669, and 4,595,670.

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Table 1 describes the operating steps and parameters of one preferred procedure used in accordance with the present invention to regenerate zeolite catalysts. The procedure is typical of those which can be employed for purposes of the present invention and is meant to be viewed as a representative example of the procedures which can be used without departing from the spirit and scope of the present invention. Included are critical conditions which must be attained to achieve maximum recovered activity.

TABLE 1

Regeneration Procedure

<u>Time</u>			<u>YPPM</u>							HCl	H ₂ O
<u>Step</u>	<u>Hrs.</u>	<u>Description</u>	<u>O₂</u>	<u>H₂O</u>	<u>HCl</u>	<u>Cl₂</u>	<u>CO₂</u>	<u>Deq.C</u>	Trap	Trap	
									<u>On</u>	<u>On</u>	
1	1.0	Dry Primary Burn	2000	0	0	0	18000	645	-	-	
2	23.0	Dry Secondary Burn	3000	0	0	0	0	645	-	-	
3	1.5	Adjust to O/C	8400	6600	0	0	0	510	-	-	
4	2.0	Oxychlorination	8400	6600	550	0	0	510	-	-	
5	4.5	Oxychlorination After Breakthrough	8400	6600	550	60	0	510	-	-	
6	4.0	Oxychlorination Cooldown	8400	6600	550	-	-	510-345	-	-	
7	3.0	Wet Air Soak	8400	6600	0	0	0	345	X	-	
8	1.0	Dry Air Soak	8400	0	0	0	0	345	X	X	
9	1.0	H ₂ Purge	0	0	0	0	0	345	X	X	
10	2.25	H ₂ Reduction (2% H ₂)	0	0	500 MAX	0	0	345	X	X	

Example 1

An extruded catalyst, produced substantially in conformance with the previous discussed methods and containing 28 wt. % alumina binder and 72% zeolite, impregnated with 0.64 wt. % platinum, was deactivated at

reforming conditions.

The catalyst was regenerated using the procedure of Table 1 except that the HCl trap 1 and drier 2 were bypassed. As a result, HCl concentration in the recycle gas rose to 650 vppm during reduction and the dryout time after wet air soak was 4 hours, both undesirably high.

The activity of the catalyst was determined when the catalyst was fresh and after the regeneration. The key measure of regeneration efficacy is recovery of at least fresh activity. The catalyst activity test (CAT) used is an accelerated test which measures activity:

The CAT test is performed at 510°C, using a feed which is 60 wt. % normal hexane and 40 wt.% methyl pentanes, at a hydrogen to feed molar ratio of 4.5 to 1.0, 98 psia hydrogen partial pressure and 8.0 whsv. The test index is % benzene yield after 46 hours. The CAT benzene yield is an accurate index of the relative activity of reforming catalysts.

The CAT benzene yield was 31.3 wt.% for the fresh catalyst and only 27.0 wt.% for the regenerated catalyst; regeneration was unsatisfactory.

This example shows that activity recovery was unsatisfactory when a zeolite catalyst was regenerated using a conventional regeneration system and procedures.

Example 2

A zeolite L reforming catalyst was deactivated at reforming conditions and regenerated in the same unit as in Example 1, using the procedure of Table 1, except that the HCl trap 1 and drier 2 were included in the recycle in the recycle gas loop.

The HCl concentration peaked at 250 vppm during reduction, and the dryout time after the wet air soak was 1.5 hours. The CAT rating of the regenerated catalyst was 32.5 wt.% benzene compared with 31.3 wt.% benzene activity for the

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fresh catalyst. With the apparatus and procedures of this present invention the activity of the catalyst was higher than for the fresh catalyst.

5 This example shows that activity recovery was satisfactory when a zeolite catalyst was regenerated using the equipment and procedures of the present invention.

10 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of the invention and, without the departing from the spirit and scope thereof, can make various changes and modifications of the invention and adapt it to various usages and conditions.

CLAIMS:

1. An apparatus for regeneration of a deactivated catalyst and redispersion of a catalytic metal in fresh catalyst, said apparatus comprising:

at least two reactors containing catalyst, means for feeding, measuring and controlling water and halogen to regenerate catalyst separately to the inlet of each reactor, means for separation of elemental halogen, a halogen-containing compound, water or mixtures thereof from a gas stream to be passed through the catalyst during a regeneration or redispersion treatment and means for removing water which is a water trap or a fixed bed drier.

2. The apparatus in accordance with claim 1, wherein said means for separation comprises means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds from said gas stream.

3. The apparatus in accordance with claim 1, wherein said means for separation comprises means for removing water from said gas stream.

4. The apparatus in accordance with claim 3, wherein said means for removing water is a fixed bed drier.

5. The apparatus in accordance with claim 4, wherein said fixed bed drier comprises a mol sieve.

6. The apparatus in accordance with claim 5, wherein said mol sieve is selected from the group consisting of a 4A mol sieve and a 5A mol sieve.

7. The apparatus in accordance with claim 6, wherein said mol sieve is a 4A mol sieve.

8. The apparatus in accordance with claim 3, wherein said means for separation

further comprises means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds from said gas stream.

9. The apparatus in accordance with claim 8, wherein said means for removing a member selected from the group consisting of elemental halogen and a halogen-containing compound is selected from the group consisting of a fixed bed adsorber, a water scrubber, and a caustic scrubber.

10. The apparatus in accordance with claim 9, wherein said means for removing a member selected from the group consisting of elemental halogen and a halogen-containing compound is a water scrubber.

11. The apparatus in accordance with claim 9, wherein said means for removing a member selected from the group consisting of elemental halogen and a halogen-containing compound is a fixed bed adsorber.

12. The apparatus in accordance with claim 11, wherein said fixed bed adsorber comprises sodium hydroxide on promoted alumina.

13. The apparatus in accordance with claim 9, wherein said means for removing a member selected from the group consisting of elemental halogen and a halogen-containing compound comprises a caustic scrubber.

14. The apparatus in accordance with claim 13, wherein said caustic scrubber comprises means for contacting said gas with caustic solution and means for removing caustic solution containing halogen from said gas stream.

15. The apparatus in accordance with claim 8, wherein said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds and said means for removing water are connected in series in a line for supplying said gas stream to said catalyst.

16. The apparatus in accordance with claim 15, wherein said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds is located upstream of said means for removing water from said gas stream in said line.

17. The apparatus in accordance with claim 16, further comprising means for reducing the temperature of said gas stream located upstream of said means for removing water in said line.

18. The apparatus in accordance with claim 17, wherein said means for reducing the temperature of said gas stream is located downstream of said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds in said line.

19. The apparatus in accordance with claim 3, further comprising means for reducing the temperature of said gas stream located upstream of said means for removing water in said line.

20. The apparatus in accordance with claim 19, wherein said apparatus further comprises a compressor with suction inlet located downstream from said means for removing water in said line.

21. The apparatus in accordance with claim 20, wherein said apparatus further comprises means for supplying at least one fluid to said line communicating between a source of said at least one fluid and said line.

22. The apparatus in accordance with claim 21, further comprising means for releasing fluid from said line communicating between said line and the ambient.

23. The apparatus in accordance with claim 22, wherein said means for releasing

is a purge line located downstream from said compressor.

24. The apparatus in accordance with claim 21, wherein said at least one fluid is at least one member selected from the group consisting of steam, hydrogen, a hydrogen halide, a source of halogen, air and an inert gas.

25. The apparatus in accordance with claim 24, wherein said at least one fluid is selected from the group consisting of steam, hydrogen, and a source of halogen.

26. The apparatus in accordance with claim 25, wherein said means for supplying said at least one fluid is located downstream from said compressor and upstream of said reactor inlets.

27. The apparatus in accordance with claim 24, wherein said at least one fluid is a gas selected from the group consisting of air, oxygen, and an inert gas.

28. The apparatus in accordance with claim 27, wherein means for supplying is located between said means for removing water from said gas stream and said compressor.

29. The apparatus in accordance with claim 28, wherein said inert gas is nitrogen.

30. The apparatus in accordance with claim 28, said apparatus further comprising:

a plurality of reactors having an inlet containing catalyst, and
means for introducing substances selected from a group of substances required for regeneration of used catalyst and substances required for predispersion of catalytic metal of fresh catalyst into the inlet of each of the reactors.

31. The apparatus in accordance with claim 30, wherein said plurality of reactors, comprise a lead reactor and a tail reactor.

32. The apparatus in accordance with claim 31, wherein said lead reactor comprises an inlet and said means for introducing said substances is operably connected to add said substances to said reactor through said inlet.

33. The apparatus in accordance with claim 32, wherein said plurality of reactors comprises a series of at least three reactors.

34. The apparatus in accordance with claim 33, comprising a supply of said substances operably connected to said means for introducing comprising at least one member selected from the group consisting of a source of steam, a source of reducing agent, and a source of halogen.

35. The apparatus in accordance with claim 34, wherein said supply of said substances comprises a source of steam, a source of hydrogen, and a source of HCl.

36. The apparatus in accordance with claim 35, wherein each of said plurality of reactors comprises an inlet.

37. The apparatus in accordance with claim 36, wherein each of said means for introducing is operably connected to add said substances through said inlet of each of said plurality of reactors.

38. The apparatus in accordance with claim 37, wherein said apparatus comprises at least one member selected from the group consisting of means for controlling, means for metering, and means for measuring concentrations of said substances operably connected to said means for introducing.

39. The apparatus in accordance with claim 38, wherein said member is a means for measuring concentrations of said substances in said stream entering the reactor.

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40. The apparatus in accordance with claim 38, wherein said member is a means for controlling the supply of said substances.

41. The apparatus in accordance with claim 38, wherein said member is a means for metering said substances.

42. The apparatus in accordance with claim 37, wherein said apparatus comprises said means for measuring, means for controlling, and means for metering said substances operably connected to said means for introducing substances.

43. The apparatus in accordance with claim 39, wherein said means for removing water is selected from the group consisted of a water trap and a fixed bed drier.

44. The apparatus in accordance with claim 43, wherein said means for removing water is a fixed bed drier.

45. The apparatus in accordance with claim 44, wherein said fixed bed drier comprises a mol sieve.

46. The apparatus in accordance with claim 45, wherein said mol sieve is selected from the group consisting of a 4A mol sieve and a 5A mol sieve.

47. The apparatus in accordance with claim 43, wherein said means for separation comprises means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds from said gas stream.

48. The apparatus in accordance with claim 47, wherein said means for removing a member selected from the group consisting of elemental halogen and a halogen-containing compound is a halogen trap.

49. The apparatus for regeneration of a deactivated catalyst in accordance with

claim 48, wherein said halogen trap comprises sodium hydroxide on promoted alumina.

50. The apparatus in accordance with claim 47, wherein said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds and said means for removing water are connected in series in a line for recycling said gas stream from said tail reactor to said lead reactor.

51. The apparatus in accordance with claim 50, wherein said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds is located upstream of said means for removing water from said gas stream in said line.

52. The apparatus in accordance with claim 51, further comprising means for reducing the temperature of said gas stream located upstream of said means for removing water in said line.

53. The apparatus in accordance with claim 52, wherein said means for reducing the temperature of said gas stream located upstream of said means for removing a member selected from the group consisting of elemental halogen and halogen-containing compounds in said line.

54. The apparatus in accordance with claim 51, wherein said apparatus further comprises a compressor located downstream from said means for removing water in said line.

55. The apparatus in accordance with claim 51, wherein said apparatus further comprises means for supplying gas to said line communicating between a source of said gas and said line.

56. The apparatus in accordance with claim 55, further comprising means for releasing fluid from said line communicating between said line and the ambient.

57. The apparatus in accordance with claim 56, wherein said means for releasing is a purge line located downstream from said compressor.

58. The apparatus in accordance with claim 55, wherein said gas is at least one member selected from the group consisting of air and an inert gas.

59. The apparatus in accordance with claim 58, wherein said inert gas is nitrogen.

60. The apparatus in accordance with claim 59, wherein means for supplying is located between said means for removing water from said inert gas stream and said compressor in said line.

61. The apparatus in accordance with claim 60, wherein said gas is an inert gas.

62. The apparatus in accordance with claim 61, wherein said inert gas is nitrogen.

63. An apparatus in accordance with claim 1, wherein said catalyst comprises a zeolite and at least one Group VIII metal.

64. The apparatus in accordance with claim 63, wherein said zeolite is a large pore zeolite.

65. The apparatus in accordance with claim 64, wherein said large pore zeolite has a pH within the range of 9.4 to 10.0.

66. The apparatus in accordance with claim 64, wherein at least 30% of said large pore zeolite is zeolite L.

67. The apparatus in accordance with claim 65, wherein at least 50% of said

zeolite L are crystallites with circular cylinders having an aspect ratio of at least 0.5.

68. The apparatus in accordance with claim 67, wherein said crystallites have a mean diameter of at least 0.2 microns.

69. The apparatus in accordance with claim 64, wherein said large pore zeolite comprises exchangeable cations.

70. The apparatus in accordance with claim 69, wherein said exchangeable cations comprise a member selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper, and a mixture of two or more members selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper.

71. The apparatus in accordance with claim 70, wherein said at least one Group VIII metal is platinum.

72. The apparatus in accordance with claim 71, wherein said exchangeable cations in said zeolite are potassium.

73. The apparatus in accordance with claim 72, wherein said exchangeable cations in said zeolite are barium.

74. The apparatus in accordance with claim 69, wherein said zeolite are in the form of aggregate particles.

75. The apparatus in accordance with claim 74, wherein said aggregate particles are members selected from the group consisting of extrudates, tablets, and spheres.

76. The apparatus in accordance with claim 75, wherein said aggregate particles comprise a binding material selected from the group consisting of metal oxide and clays.

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77. The apparatus in accordance with claim 76, wherein said binder material is a member selected from the group consisting of alumina, silica and alumina-silicates.

78. The apparatus in accordance with claim 63, wherein said catalyst is non-acidic and monofunctional.

79. A process for treating catalyst comprising at least one Group VIII metal and contained in at least two reactors, comprising exposing the catalyst to a gas comprising halogen so as to redisperse said metal, wherein said exposing comprises initiating a flow of halogen to each of said reactors, first to the reactor requiring the longest oxychlorination time and adjusting the halogen flow rate through said reactors so that halogen break-through from said reactors is substantially simultaneous, and reducing the metal in the reactors one at a time moving from tail reactor to lead reactor.

80. The process as defined by claim 79, wherein said breakthrough from said reactors results in less than two hours.

81. The process as defined by claim 79, comprising adjusting said halogen flow rate through each of said reactors so as to result in substantially simultaneous halogen breakthrough for all of said reactors in accordance with the following equation:

$$T = W/R \cdot K$$

wherein W is the weight of the catalyst in each of said reactors, R is the weight rate of halogen flow, T is the oxychlorination time and K is a constant that is characteristic of the catalyst and the units selected to express weight and time.

82. The process as defined by claim 81, wherein said plurality of said reactors include at least three reactors, one of said reactors containing a heaviest weight of catalyst and another of said reactors containing a lightest weight of catalyst.

83. The process as defined by claim 82, wherein said initiating comprises

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introducing halogen flow first to said one of said reactors containing said heaviest weight of catalyst and last to said another of said reactors containing said lightest weight of said catalyst.

84. The process as defined by claim 83, wherein said at least three reactors include a lead reactor and a tail reactor.

85. The process as defined by claim 84, wherein said one of said reactors containing said heaviest weight of catalyst comprises said tail reactor.

86. The process as defined by claim 85, wherein another of said reactors containing said lightest weight of catalyst comprises said lead reactor.

87. The process as defined by claim 86, wherein said initiating comprises introducing halogen flow first to said tail reactor.

88. The process as defined by claim 87, wherein said initiating comprises introducing halogen flow last to said lead reactor.

89. The process as defined by claim 81, wherein said halogen is selected from the group consisting of sources of chlorine.

90. The process as defined by claim 89, wherein said sources of chlorine are selected from the group consisting of Cl_2 , HCl , chloroform, methyl chloride, carbon tetrachloride, 1, 2-dichloroethane, trichloroethane, and mixture of one or more members selected from the group consisting of Cl_2 , HCl , chloroform, methyl chloride, carbon tetrachloride, 1, 2-dichloroethane and trichloroethane.

91. The process as defined by claim 90, wherein a source of chlorine is HCl .

92. The process as defined by claim 91, wherein said catalyst comprises a

zeolite.

93. The process as defined by claim 92, wherein said zeolite is large pore zeolite.

94. The process as defined by claim 93, wherein at least 30% of said large pore zeolite is zeolite L.

95. The process as defined by claim 94, wherein one of said at least one Group VIII metal is platinum.

96. The process as defined by claim 94, wherein said zeolite comprises exchangeable cations.

97. The process as defined by claim 96, wherein said at least one Group VIII metal is platinum.

98. The process as defined by claim 94, wherein at least 50% of said zeolite L are crystallites with circular cylinders having an aspect ratio of at least 0.5.

99. The process as defined by claim 98, comprising exchangeable cations selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper, and a mixture of two or more members selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper.

100. The process as defined by claim 99, wherein said at least one Group VIII metal is platinum.

101. The process as defined by claim 99, wherein said exchangeable cations in said zeolite is at least one member selected from the group consisting of potassium and

barium.

102. The process as defined by claim 101, wherein said exchangeable cations are potassium.

103. The process as defined by claim 102, wherein said exchangeable cations are barium.

104. The process as defined by claim 101, wherein said zeolite are in the form of aggregate particles.

105. The process as defined by claim 104, wherein said aggregate particles are members selected from the group consisting of extrudates, tablets, and spheres.

106. The process as defined by claim 105, wherein said aggregate particles comprise a binder selected from the group consisting of metal oxides and clays.

107. The process as defined by claim 106, wherein said binders are members selected from the group consisting of alumina, silica and alumina-silicates.

108. The process as defined by claim 91, wherein said catalyst is non-acidic and monofunctional.

109. A process as defined by claim 79, for treating a zeolite-based catalyst comprising at least one Group VIII metal contained in a plurality of reactors including a lead reactor and a tail reactor comprising:

 exposing catalyst comprising catalytic metal selected from the group of Group VIII metals in an unreduced state contained in one of said reactors to a gas stream containing a reducing agent to substantially completely reduce said Group VIII metal; and

 maintaining catalyst comprising said catalytic metal in an unreduced state contained in other said reactors in an atmosphere substantially devoid of at least one

member selected from the group consisting of halogen and water.

110. The process as defined by claim 109, further comprising:

introducing a gas stream containing a reducing agent into another of said reactors containing catalyst comprising said catalytic metal in an unreduced state and exposing said catalytic metal to substantially completely reduce said catalytic metal while maintaining catalyst comprising said catalytic metal in an atmosphere substantially devoid of at least one member selected from the group consisting of halogen and water until catalyst comprising said catalytic metal in each of said reactors is substantially completely reduced whereby said catalyst metal is only exposed to a halogen subsequent to being reduced.

111. A process in accordance with claim 110, wherein said plurality of reactors include a lead reactor and a tail reactor and wherein said exposing comprises introducing a gas stream which is substantially devoid of at least one member selected from the group consisting of halogen, halogen-containing compounds, and water to said tail reactor; passing said gas stream through said tail reactor; subsequently introducing said gas stream to said lead reactor; and passing said gas stream through said lead reactor until said catalytic metal of said catalyst contained in said lead reactor is substantially completely reduced.

112. The process as defined by claim 111, wherein said plurality of reactors are a series of reactors comprising at least one intermediate reactor positioned between said lead reactor and said tail reactor and said introducing said gas stream to each said reactor is performed sequentially first through said tail reactor until reduction of said catalytic metal of said catalyst contained in said tail reactor is substantially complete; next introducing and passing said gas stream through each said at least one intermediate reactor until reduction of said catalytic metal of said catalyst contained in each said intermediate reactor is sequentially substantially complete; and finally introducing and passing said gas stream through said lead reactor until reduction of said catalytic metal of said catalyst contained in said tail reactor is substantially complete.

113. The process as defined by claim 112, comprising discharging a gas stream from said tail reactor comprising HCl and water and introducing a gas stream substantially devoid of HCl and water to said lead reactor.

114. The process as defined by claim 113, comprising removing HCl and H₂O from the discharged gas stream before reintroducing said gas stream substantially devoid of HCl and water into said lead reactor.

115. The process as defined by claim 109, comprising removing water from said discharged gas stream.

116. The process as defined by claim 115, wherein said removing water comprises passing said gas stream through means for removing water.

117. The process as defined by claim 116, wherein said means for removing water is a water trap.

118. The process as defined by claim 117, wherein said water trap is a mol sieve selected from the group consisting of a 4A mol sieve and 5A mol sieve.

119. The process as defined by claim 118, wherein said removing water results in a substantially dry gas stream and said exposing comprises introducing said substantially dry gas stream into said lead reactor.

120. The process as defined by claim 114, wherein said removing HCl comprises passing said discharged gas stream through means for removing HCl from said gas discharged stream to result in a gas stream substantially devoid of HCl.

121. The process as defined by claim 120, wherein said means for removing HCl is an HCl trap.

122. The process as defined by claim 121, wherein said HCl trap comprises sodium hydroxide on promoted alumina.

123. The process as defined by claim 122, comprising removing water from said discharged gas stream substantially devoid of HCl.

124. The process as defined by claim 123, wherein said removing water comprises passing said discharged gas stream substantially devoid of HCl through means for separating water from said discharged gas stream.

125. The process as defined by claim 124, wherein said means for separating water comprises a water trap.

126. The process as defined by claim 125, wherein said water trap comprises a mol sieve.

127. The process as defined by claim 126, wherein said mol sieve is selected from the group consisting of a 4A mol sieve and a 5A mol sieve.

128. The process as defined by claim 124, comprising reducing the temperature of said gas stream substantially devoid of HCl to result in a cooled gas stream prior to passing said cooled gas stream through said means for separating water from said gas stream.

129. The process as defined by claim 109, further comprising exposing deactivated catalyst contained in said reactors to oxygen and halogen in order to redisperse said metal and result in substantially simultaneous halogen breakthrough for all of said reactors.

130. The process as defined by claim 129, wherein said exposing comprises

initiating halogen flow at a flow rate to each of said reactors and adjusting the halogen flow rate through said reactors so that halogen breakthrough is substantially simultaneous from each of said reactors.

131. The process as defined by claim 130, comprising recycling said halogen flow for between 1-4 hours after said breakthrough from said reactors.

132. The process as defined by claim 131, wherein at least three of said plurality of reactors contain a different weight of said catalyst, one of said reactors containing a heaviest weight of catalyst and another of said reactors containing a lightest weight of catalyst, wherein said exposing comprises initiating a flow of halogen to each of said reactors and adjusting the halogen flow rate through each said reactor so that halogen breakthrough from the reactors is substantially simultaneous.

133. The process as defined by claim 132, wherein said initiating comprises introducing halogen flow first to said one of said reactors containing said heaviest weight of catalyst and last to said another of said reactors containing said lightest weight of said catalyst.

134. The process as defined by claim 133, wherein said at least three reactors include a lead reactor and a tail reactor.

135. The process as defined by claim 134, wherein said one of said reactors containing said heaviest weight of catalyst is said tail reactor.

136. The process as defined by claim 135, wherein another of said reactors containing said lightest weight of catalyst comprises said lead reactor.

137. The process as defined by claim 136, wherein said initiating comprises introducing halogen flow first to said tail reactor.

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138. The process as defined by claim 137, wherein said initiating comprises introducing halogen flow last to said lead reactor.

139. The process as defined by claim 138, wherein said halogen is selected from the group consisting of sources of chlorine.

140. The process as defined by claim 139, wherein said sources of chlorine are selected from the group consisting of Cl_2 , HCl , chloroform, methyl chloride, carbon tetrachloride, 1,1-2 dichloroethane, trichloroethane, and mixture of one or more members selected from the group consisting of Cl_2 , HCl , chloroform, methyl chloride, carbon tetrachloride, 1,1-2 dichloroethane and trichloroethane.

141. The process as defined by claim 140, wherein said source of chlorine is HCl .

142. The process as defined by claim 109, wherein said catalyst comprises a zeolite.

143. The process as defined by claim 142, wherein said zeolite is a large pore zeolite.

144. The process as defined by claim 143, wherein at least 30% of said large pore zeolite is zeolite L.

145. The process as defined by claim 143, wherein said zeolite L has a pH within the range of about 9.4 to 10.0.

146. The process as defined by claim 143, wherein at least 50% of said zeolite L are crystallites with circular cylinders having an aspect ratio of at least 0.5.

147. The process as defined by claim 146, wherein said crystallites have a mean

diameter of at least 0.2 microns.

148. The process as defined by claim 143, wherein said large pore zeolite comprises exchangeable cations.

149. The process as defined by claim 148, comprising exchangeable cations selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper, and a mixture of two or more members selected from the group consisting of potassium, sodium, strontium, barium, calcium lithium, magnesium, rubidium, cesium and copper.

150. The process as defined by claim 149, wherein said at least one Group VIII metal is platinum.

151. The process as defined by claim 150, wherein said exchangeable cations in said zeolite is a member selected from the group consisting of potassium and barium.

152. The process as defined by claim 151, wherein said exchangeable cations are potassium.

153. The process as defined by claim 151, wherein said exchangeable cations are barium.

154. The process as defined by claim 153, wherein said zeolite are in the form of aggregate particles.

155. The process as defined by claim 154, wherein said aggregate particles are members selected from the group consisting of extrudates, tablets, and spheres.

156. The process as defined by claim 155, wherein said aggregate particles comprise a binding selected from the group consisting of metal oxide binders and clays.

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157. The process as defined by claim 156, wherein said binders are members selected from the group consisting of alumina, silica and alumina-silicates.

158. The process as defined by claim 157, wherein said catalyst is non-acidic and monofunctional.

