

REPLACED SHEETS		SG
☒	Description	: paged ...1... to paged ...21....
☒	Claim(s)	: paged ...21... to paged ...44....
☐	Drawing(s)	: paged to paged
☐	Abstract	: paged to paged
DATE OF RECEIPT		

PCT/US93/08555

This Sheet Has Been Replaced



1

**REGENERATION OF SEVERELY
DEACTIVATED REFORMING CATALYSTS**

5

1. Field of the Invention

This invention relates to regeneration of deactivated hydrocarbon processing catalysts comprising catalytic metals dispersed in a zeolite, particularly but not exclusively, reforming catalysts including one or more Group VIII metals in a large pore zeolite, such as platinum in zeolite L. The process of this invention is particularly effective for regenerating catalysts which have been more severely deactivated than is usual, for example, due to process upsets or to multi-cycle of on-oil regeneration operations. Such, catalysts regenerated in accordance with the present invention have been found to recover more of their activity and selectivity than if they were regenerated using conventional procedures. The general principles of the inventive process comprise (i) increasing the severity and time of the coke burn, (ii) using a source of high partial pressure chlorine in the oxychlorination step to redisperse catalytic metal e.g., platinum, (iii) improving chlorine removal by a wet, high temperature post treatment, at low pressure and (iv) enhancing reduction of catalytic metal by using high temperature at low pressure.

2. Background

Catalytic reforming is a major petroleum refining process used to raise the octane rating of naphthas (C_6 to C_{11} hydrocarbons) for gasoline blending. Catalytic reforming is also a principal source of aromatic chemicals, i.e., benzene, toluene and xylenes, via conversion of paraffins and naphthenes to aromatics.

The principal reforming chemical reactions are

dehydrogenation of cyclohexane to aromatics, dehydrocyclization of paraffins to aromatics, dehydroisomerization of alkylcyclopentanes to aromatics, isomerization of normal paraffins to
5 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.

10 Reforming is typically carried out at temperatures of 426° to 538°C (800°F to 1000°F), pressures of 0.34 to 20.7 MPa (50 to 3000 psi), hourly weight space velocities of 0.5 to 3.0, and in the presence of hydrogen at molar ratios to feed of 1 to 10. Other
15 characteristics of reforming processes are well known in the art, and reference is made to US-A-4,914,068 for further teachings on this topic.

Catalysts currently used in commercial reformers include a Group VIII metal, such as platinum, or
20 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 reforming catalysts are suitable for aromatizing C₈+ paraffins,
25 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 reforming catalysts are bifunctional,
30 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.

35 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.

Compared to conventional alumina based reforming catalysts which are acidic and bifunctional, zeolite based catalysts such as zeolite L are non-acidic and monofunctional, which gives advantages in reforming light naphtha.

For production line-scale reforming processes, zeolite is preferably formed into aggregates, such as extrudates or tablets, typically 0.08 - 0.65 cm. in size; 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.

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. Platinum-on-zeolite L reforming catalysts are uniquely active and selective for aromatizing paraffinic C₆'s, C₇'s and C₈'s. Catalyst activity decreases progressively with time on oil due to build up of coke deposits on the catalyst and agglomeration of platinum, and although reactor inlet temperatures are periodically raised to compensate for declining activity, periodically, the catalyst must be regenerated to recover its initial activity.

In general, such regeneration procedures include: 1) burning off the coke deposits using oxygen, 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.

For example, it is known that coke deposits may be removed from such catalysts by heating them in the presence of dilute oxygen at a flame-front temperature of 430°C to 540°C. This combustion may be preceded by flushing out residual hydrocarbon with inert gas, such as nitrogen. High temperature decoking however leads to loss of surface area of the supported metal particles and to removal of platinum from the zeolite channels, thereby resulting in loss of catalyst activity. Thus, after combustion, the catalyst is

This Sheet Has Been Replaced



often subjected to oxychlorination by contact with oxygen and chlorine, or a chlorinated compound, such as CCl_4 , at elevated temperatures.

5 In attempts to overcome problems experienced during regeneration of large-pore zeolite-based reforming catalysts, various procedures have been developed.

10 US-A-4,851,380 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 metal into large agglomerates and then treating the catalyst with a halogen acid gas to remove sulfur contaminants.

15 US-A-4,914,068 contains useful discussion on oxychlorination of decoked zeolite catalysts. However, the chlorine concentrations taught therein, at the specified total pressures, equate to extremely low chlorine or HCl partial pressures which do not give the advantages of the instant invention. Moreover, US-A-
20 4,914,068 requires a reduction step practiced at a temperature which is lower than that of the chlorination or oxychlorination step, and discloses the benefits of cooling the catalyst in the presence of
25 oxygen before the reduction.

US-A-4,925,819, teaches 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. Such procedures
30 adequately recover the activity of catalysts which are normally deactivated. However, it has been found that by use of such procedures, selectivity of regenerated catalysts are typically about 5% to about 10% lower than fresh catalysts. Even with diligent operation,
35 reformers sometimes go into upset condition which



severely deactivate the catalyst. Examples of upset conditions include loss of hydrogen flow or high temperature excursions due to excessive cracking reaction. Notwithstanding the disclosed effectiveness of the procedures of US-A-4925819, these procedures still do not fully recover the activity of severely deactivated catalysts. However, it has now been found that by incorporating certain critical modifications as listed above, the procedure of the present invention is capable of regenerating severely deactivated catalysts, and also, surprisingly, of achieving better selectivity with normally deactivated catalysts.

SUMMARY OF THE INVENTION

15

According to the present invention there is provided a process for regenerating a deactivated catalyst comprising a Group VIII catalytic metal and zeolite, which process comprises:

20

a) contacting the deactivated catalyst with a gaseous stream comprising oxygen, inert gas and water under oxidation conditions comprising a temperature of from 400°C to 600°C for a time sufficient to burn coke off the deactivated catalyst and convert the metal to agglomerated particles which are accessible to chlorine-containing gas in subsequent process step (b), to result in a substantially decoked catalyst;

25

b) contacting the substantially decoked catalyst with a gaseous stream comprising water, a source of chlorine, oxygen and an inert gas under oxychlorination conditions comprising a temperature of from 450°C to 550°C and a partial pressure of chlorine derived from the source of chlorine which is greater than 207 Paa (0.03 psia) for a time sufficient for hydrogen chloride and/or chlorine to breakthrough the

35

This Sheet Has Been Replaced



catalyst to an HCl + Cl₂ partial pressure greater than 138 Paa (0.02 psia) so as to chlorinate and disperse the metal and result in a chlorinated catalyst comprising substantially completely dispersed chlorine-complexed metal;

5 c) contacting the chlorinated catalyst with a gaseous stream comprising water, oxygen, and an inert gas under chlorine removal conditions comprising a temperature of from 450°C to 550°C, a low total
10 pressure, and a time effective to remove from the chlorinated catalyst at least some of the chloride complexed to the metal and result in a gaseous stream after contact with the catalyst comprising hydrogen chloride at a partial pressure of less than 27.6 Paa
15 (0.004 psia); and

d) contacting the chlorinated catalyst from step (c) with a gaseous stream comprising inert gas, hydrogen (and optionally water) under reducing conditions comprising a low total pressure and a
20 temperature of from 350°C to 550°C for a time effective to reduce at least some of the chlorine-complexed metal in the catalyst to the metallic state and result in a regenerated catalyst comprising dispersed metal and zeolite.

25 The innovative modifications in the regeneration procedure of the present invention, over the previously identified regeneration procedures, include: (i) increased severity and time of coke burn, i.e., running the coke burn longer and at significantly more severe
30 conditions; (ii) use of a source of chlorine capable of yielding chlorine at a partial pressure of greater than 207 Paa (0.03 psia), such as elemental chlorine, i.e., Cl₂, HCl or other chlorine-containing agent to oxychlorinate and to redisperse the metal, preferably
35 Pt; (iii) improved Cl removal after oxychlorination by



operating at high temperature, and at low pressure, i.e., performing the postoxychlorination treatment at higher temperature to strip off more residual chlorine; and (iv) enhanced metal e.g., Pt reduction by operating at high reduction temperature to complete reduction of the metal e.g., platinum to the zero valent state and reducing at low pressure. In addition, the decoked catalyst may be reduced with hydrogen before step (b), in which case an inert purge step may be required after the hydrogen reduction and before oxychlorination in step (b). The improved regeneration procedure of the present invention may be conducted at a pressure of from sub atmospheric to 2.07 MPaa (300 psia), although steps (c) and (d) are conducted at low partial pressures to ensure appropriate stripping of chloride from the catalyst. The concentrations of the gases used depend upon the operating pressure and are adjusted accordingly to yield a desired range of partial pressure of the gas component wherein the partial pressure of gas A = the concentration of A x the total pressure.

Although not wishing to be bound by any particular theory, we believe that in practice of prior art regeneration techniques, the reactive gases in the oxychlorination step do not get access to all the catalytic metal e.g., Pt particles inside the zeolite channels in a severely deactivated catalyst. It is believed that increasing the severity of the coke burn step, as required by step (a) of the invention, permits the Group VIII catalytic metal to be accessible to subsequent treatment with chlorine-containing gas because of expulsion of the metal, e.g., of platinum, from within the microchannels of the zeolite. This step also clears the microchannels of foreign matter such as refractory (difficult to remove) coke which, if



not removed, would interfere with reforming reactions. The metal, e.g., platinum, agglomerates outside the zeolite into particles which have been found to be larger than with prior art procedures. The presence of
5 a substantial proportion, e.g., greater than 80 or 90% by weight, of the metal in the form of particles greater than 200 Angstrom in size has been found to indicate that the metal has been cleared from the microchannels and is accessible by the chlorine gas in
10 step (b). Thus in accordance with the invention the zeolite has channels containing particles of Group VIII metal, and the temperature and the time of the oxidation conditions of step (a) are sufficient to remove a substantial amount of the particles of metal
15 from inside to outside the channels in the zeolite, preferably to the extent that the metal outside the channels is in the form of agglomerated particles, having a size greater than about 200Å. The catalytic metal is preferably platinum, although references
20 hereinafter to platinum should be taken as equally applicable to other Group VIII metals.

In step (b), chlorine at high concentration is required to decompose and redisperse these larger metal e.g., platinum, particles. With more aggressive
25 chlorination it is necessary to enhance the post treat step (c) and platinum reduction step (d) to ensure adequate removal of residual chlorine and complete reduction of catalytic metal.

In addition to required steps (a), (b), (c) and
30 (d), other process steps are optionally employed. Thus according to one embodiment, between steps (a) and (b) there is performed an intermediate reducing step (a') comprising contacting the substantially decoked catalyst with a gaseous stream comprising inert gas and
35 hydrogen under reducing conditions for a time effective



to reduce the metal component of the catalyst to the metallic state.

According to another embodiment, between steps (c) and (d) there is performed a purging step (c') comprising contacting the chlorinated catalyst from step (c) with an oxygen-free displacement gas flow for a time sufficient to purge oxygen therefrom prior to performing step (d).

10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The improved regeneration procedure of the present invention has four distinct steps: a) coke burn, b) oxychlorination, c) stripping, and d) hydrogen reduction.

15 (a) coke burn step

Step (a) is preferably performed at a temperature greater than 510°C and/or at an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or at a water partial pressure not greater than 10.3 kPaa (1.5 psia) and/or at a total pressure of from sub-atmospheric to 2.07 MPaa (300 psia). Preferably, the temperature is from 520°C - 600°C, more preferably 530°C - 550°C, with 530°C - 540°C being most preferred. The coke burn step should ideally be conducted for a time longer than about 6 hours, e.g. 10 - 100 hours, more preferably 36 - 80 hours, with 48 - 75 hours being more preferred and 60 - 75 hours being most preferred. In this step, the partial pressure of water is preferably up to 5.2 kPaa (0.75 psia), and is more preferably from 1.38 to 5.2 kPaa (0.2 to 0.75 psia), and most preferably from 1.38 to 3.45 kPaa (0.2 to 0.5 psia).

Preferably, step (a) is performed for a period of time until the gaseous stream after contact with the catalyst comprises a partial pressure of carbon dioxide



of less than 69 Paa (0.01 psia), more preferably less than 27.6 Paa (0.004 psia). In a preferred embodiment, step (a) is performed in a first stage (a1) and a second stage (a2) wherein stage (a1) is performed at a lower temperature e.g., 400 - 500°C, than stage (a2), e.g., 520-600°C.

(b) oxychlorination step

In this stage, the substantially decoked catalyst is treated with a second wet oxychlorination gas stream comprising chlorine from a source of chlorine yielding chlorine at a high partial pressure, preferably from 207 Paa to 2.07 kPaa (0.03 to 3 psia), more preferably 348 Paa to 6.9 kPaa (0.05 to 1.0 psia), and most preferably 690 Paa to 3.45 kPaa (0.1 to 0.5 psia).

In a preferred embodiment, step (b) is performed at a temperature of from 480°C to 550°C and/or at an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or at a water partial pressure of not greater than 10.3 kPaa (1.5 psia) and/or at a total pressure of from sub-atmospheric to 2.07 kPaa (300 psia) and/or for at least two hours after HCl and/or Cl₂ breakthrough.

(c) wet post oxychlorination stripping step

In this stage, excess chlorine is removed from the chlorinated catalyst using a third wet gaseous stream, preferably at a temperature of from 480 to 520°C and/or at a water partial pressure not greater than 10.3 kPaa (1.5 psia), more preferably from 348 Paa to 2.76 kPaa (0.05 to 0.4 psia) and/or at an oxygen partial pressure of less than 31 kPaa (4.5 psia), more preferably from 4.83 to 20.7 kPaa (0.7 to 3 psia). The total pressure of step (c) is required to be low, and is preferably below 690 kPaa (100 psia) e.g., from sub-atmospheric to 448 kPaa (65 psia), most preferably at about atmospheric pressure. The step is preferably performed for a time sufficient to effect a chloride



concentration in offgas from the chlorinated catalyst of less than about 200 vppm at one atmosphere, which corresponds to a partial pressure of about 20.7 Paa (0.003 psia) more preferably at an offgas HCl concentration of less than 10.3 Paa (0.0015 psia).

(d) reduction step

In this stage, chlorinated catalyst from which excess chlorine has been removed is reduced by exposure to a fourth wet gaseous stream. Preferably step (d) is performed at a hydrogen partial pressure greater than 103 Paa (0.015 psia) e.g., from 103 Paa to 34.5 kPaa (0.015 to 5 psia), and/or a water partial pressure not greater than 10.3 kPaa (1.5 psia), e.g., 348 Paa to 2.76 kPaa (0.05 to 0.4 psia), and/or at a temperature of from 450°C to 520°C more preferably, 480° to 520°C. The total pressure of step (d) is required to be performed at a low total pressure, preferably below 690 kPaa (100 psia), more preferably from sub-atmospheric to 448 kPaa (65 psia), most preferably at about atmospheric pressure. In a preferred embodiment, step (d) is performed under conditions such that the gaseous stream after contact with the catalyst comprises hydrogen chloride at a partial pressure of less than 51.7 Paa (0.0075 psia).

In addition to the foregoing, purge steps may be used between any of the previously described stages as desired or as deemed to be necessary from the standpoints of safety and technology. In this regard, an inert gas e.g., nitrogen purging step should ideally be used before reduction to remove oxygen from the reactor to avoid forming an explosive gas mixture. Also, the optional hydrogen reduction step (a') may be used after step a) but before step b) in which case the reduction with hydrogen should ideally be preceded and followed with a purging of an inert gas, such as



nitrogen, before step b).

It will be understood that within each of steps (a) - (d) and the optional additional steps, there are several parameters (e.g., temperature, pressure, partial pressure, end points, concentrations) which may be varied within the required ranges in order to control the procedure and effect of the regeneration process. For ease of understanding of the scope of the invention, these parameters have been listed as "ranges of conditions" in Table 1. In this table the ranges of conditions given for each parameter of each process step are intended to be read independently of the ranges given for every other parameter. Those ranges indicated as suitable are intended to be understood as indicating those exemplary ranges which may be employed in performance of the invention, and not as any delineation of the scope of the invention. Further description of the preferred means of implementing the inventive process is provided hereinafter, and this should be read in conjunction with the "ranges of conditions" of Table 1.

a) Coke burn: The purpose of the coke burn step is to remove carbonaceous materials which accumulate on the catalyst during hydrocarbon processing off the catalyst by oxidizing it. The coke burn is best conducted in two phases - a primary coke burn (a1) followed by a secondary coke burn (a2). The primary coke burn is done at less severe conditions (lower temperature and lower inlet oxygen concentration) than the secondary coke burn. This is because thermal excursions to excessively high temperatures can occur if heavily coked deactivated catalyst were exposed to severe coke burn conditions directly.

As a practical matter, prior to regeneration of a deactivated catalyst, the reactors are purged to remove

This Sheet Has Been Replaced



residual hydrocarbons left in the reactors when the hydroprocessing operation is terminated. This may be done by establishing a flow of hydrogen to the reactors and continuing hydrogen flow until hydrocarbon is displaced by hydrogen. Then flow of an inert gas such as nitrogen is established through the catalyst beds and maintained to purge the hydrogen. Linear gas velocity is maintained above about 15.2 cm/sec (0.5 FPS) for the purges and the coke burn and for all subsequent steps in the regeneration procedure. The inert gas flowing to the inlet of the reactors during the first stage of the coke burn step (a1) is heated to temperature using the feed preheater furnace. A gas stream comprising low concentrations of oxygen (Table 1) and an inert gas is used in the primary coke burn to avoid excessively high temperature, because of adiabatic coke burn condition. Under adiabatic coke burn, the increase in the flame front temperature depends solely on oxygen concentration regardless of the total pressure. High oxygen concentration can be used in primary coke burn when the coke burn is not carried out at the adiabatic condition, e.g. an external cooling to the reactor is available or a higher heat capacity inert gas other nitrogen is used. The primary coke burn step (a1) is preferably continued until the molar ratio of carbon dioxide to oxygen in the reactor outlet gas falls to about 3:1. The time to complete the primary coke burn phase varies with the concentration of coke on the catalyst, space velocity, and oxygen concentration in the reactor inlet gas and can take between five and fifty hours. The first gaseous stream in this stage of the process may be substantially dry or contain an amount of water at a partial pressure taught in Table 1.

The secondary coke burn step (a2) is initiated by



raising inlet inert gas temperature to above 510°C, and raising inlet oxygen concentration to yield an oxygen partial pressure as taught in Table 1. Water is introduced to the reactor inlet gas stream to yield water partial pressure as taught in Table 1. In this regard, when the first stage burn is carried out at a lower water partial pressure than the second stage coke burn, it is preferred that the catalyst be saturated with the higher water partial pressure used in the second coke burn before increasing the temperature. Preferred temperatures, times, end points and pressures are as taught in Table 1. Lower and higher total pressures may be used when the concentrations of gases are adjusted accordingly to yield equivalent partial pressures of the gas component wherein the partial pressure of gas A = the concentration of A x the total pressure.

In addition to removing essentially all the coke from the catalyst, a second important purpose of the coke burn step is to expel the catalytic metals in zeolite microchannels to the outside surfaces of the catalyst and as a consequence the catalytic metal is agglomerated into particles which are typically larger than about 200 Å. The substantial removal of catalytic metal from inside the zeolite channels is assured by conducting the secondary coke burn phase at a temperature above 510°C with water present for at least 6 hours. Although not wishing to be bound by any particular theory, it is believed that the severe agglomeration conditions clears the zeolite microchannels of detritus such as refractory coke, and improves access to the catalytic metals for subsequent redispersion.

The effluent gas, i.e., the gas stream from the outlet of the vessel containing the catalyst, can be



recycled during coke burn. If it is recycled then a fraction of the effluent gas must be purged and replaced with fresh inert gas to remove combustion products from the system. The purge rate is typically
5 5% to 30% of the recycle gas rate.

b) Oxychlorination: The purpose of the oxychlorination step is to redisperse the catalytic metals back into the zeolite microchannels by converting the metals to their chlorides. The metal
10 chlorides are mobile and distribute facilely over the catalyst surfaces.

In the process of this invention, redispersion is accomplished by treating the decoked catalyst with a gas stream containing chlorine from a source of
15 chlorine, oxygen, and water. Preferably the source of chlorine comprises organochloride compounds, elemental chlorine, and HCl. Preferred organochloride compounds comprise carbon tetrachloride, chloroform, methyl chloride, methylene chloride, dichloroethane,
20 trichloroethane, and dichloroethylene, and mixtures thereof. Preferably the source of chlorine is Cl_2 , HCl, or CCl_4 , most preferably Cl_2 . The oxychlorination step is conducted suitably at a total pressure at or above atmospheric pressure, as shown in Table 1. The
25 concentrations of oxygen, water, and chlorine-containing compound injected at the reactor inlet are adjusted according to the reactor total pressure to yield the respective reactor inlet partial pressures, as shown in Table 1, wherein the partial pressure of
30 gas A = the concentration of gas A x the total pressure.

The oxychlorination is continued at least until HCl and/or chlorine appears in the reactor outlet gas stream at a partial pressure greater than about 138 Paa
35 (0.02 psia) which is referred to herein as the



"breakthrough" of HCl and/or chlorine. After breakthrough, it is preferred to continue oxychlorination for two to four hours to make sure all the catalyst is thoroughly oxychlorinated.

5 c) Stripping: The purpose of stripping is to remove excess chlorine from the catalyst. Chlorine evolves during the subsequent hydrogen reduction step as HCl and induces agglomeration of the catalytic metal particles in proportion to HCl partial pressure.
10 Accordingly, within limits, the more chlorine stripped from the catalyst prior to reduction, the higher will be the activity of the regenerated catalyst.

To improve the removal of chlorine, stripping is done at low pressure e.g., about atmospheric pressure.
15 Total pressure and component partial pressures are as shown in Table 1. Stripping is continued until the HCl partial pressure in the reactor offgas falls below the levels shown in Table 1. This typically can take between about one and thirty hours. As previously
20 mentioned, oxygen flow to the catalyst is terminated and the flow of wet inert gas is continued for a time to thoroughly purge oxygen from the system prior to introducing H₂.

To promote and enhance the efficiency of chlorine
25 evolution, it is important that the stripping step be done at as low a pressure as practicable. In most cases this is about atmospheric pressure; however, stripping can be enhanced by pulling vacuum on the reactors. Also, it is important to maintain a
30 temperature of at least about 450°C, preferably within the ranges shown in Table 1. However, stripping may be carried out at higher reactor pressure with reduced stripping efficiency and therefore requires a longer time of stripping.

35 The effluent gas, i.e., the gas stream from the



outlet of the vessel containing the catalyst, can be recycled. If it is recycled then a fraction of the effluent gas must be purged and replaced with fresh inert gas. The purge rate is typically 5% to 30% of the recycle gas rate. Ideally, though, this step is once through.

d) Reduction: The final step is reduction of catalytic metals, e.g., platinum, now dispersed uniformly across the surfaces of the catalyst as chlorides, to small zero valent metal clusters.

This is accomplished by exposing the stripped catalyst to hydrogen at a temperature greater than about 450°C, preferably within the range as shown in Table 1. Oxygen left in the stripping step is purged with inert gas, such as nitrogen, down below the explosion limit prior to introducing hydrogen. The reduction is accomplished with a gas stream containing hydrogen having a preferred partial pressure of hydrogen greater than 103 Paa (0.015 psia), preferably within the range shown in Table 1. The gas stream at the reactor inlet for the hydrogen reduction step also may contain water at a partial pressure as shown in Table 1, and the reduction is preferably conducted for a period of one to two hours. Although the exact reduction conditions used may vary, higher regenerated catalyst activity is achieved when the reduction temperature is over 450°C. Hydrogen feed rate is controlled such that the partial pressure HCl in reactor offgas does not exceed 51.7 Paa (0.0075 psia). Preferably, the reduction step (d) is performed at a reactor total pressure of atmospheric to 448 Paa (65 psia), and preferably at about atmospheric. However, reactor pressure higher than 448 Paa (65 psia) may be used in this reduction step. For an easy operation, it is preferably to operate this reduction step at the



same pressure as the previous stripping step.

In this hydrogen reduction step, hydrogen and inert gas may be recycled to the reactor inlet with a 10 to 30% purge. Preferably, this reduction step is carried out without recycle. In such embodiment, however, the catalyst has to be dried out after wet reduction in step (d) and before introducing hydrocarbon feed into the reactor with a drying gas comprising e.g., nitrogen or hydrogen, to a preferred water partial pressure of less than 27.6 Paa (0.004 psia), more preferably less than 20.7 Paa (0.003 psia), and most preferably less than 10.3 Paa (0.0015 psia). This drying step, therefore, is accomplished by reducing the partial pressure of water in the gas stream introduced at the inlet of the vessel containing the catalyst through the introduction of the drying gas so as to result in a reduced partial pressure of water in the gas at the outlet. Thus, the gas at the outlet is substantially devoid of water.

As previously mentioned, an optional hydrogen reduction step may be introduced after step (a) and before step (b).

As previously discussed, before hydrogen is introduced, however, oxygen remaining in the reactor after the coke burn must be purged from the reactor to preclude forming combustible mixtures of hydrogen and oxygen. In this stage, oxygen purging is preferably accomplished by cutting off oxygen flow and continuing nitrogen flow through the reactors.

For purposes of the present invention, feeding nitrogen for about 30 minutes to about two hours, with one hour being most preferred, at a temperature of about 510°C and a pressure within the range of between about atmospheric and 2.07 MPaa (300 psia) are suitable for reducing oxygen concentration to a safe level; and

This Sheet Has Been Replaced



the nitrogen linear velocity is maintained in the catalyst beds at least about 15.2 cm/sec (0.5 FPS) to achieve adequate gas distribution and gas/solid contacting.

- 5 Hydrogen reduction step (a') is initiated by starting flow of hydrogen into the nitrogen flowing into the reactors. Conditions of hydrogen reduction can be varied over a wide range, as shown in Table 1.

- 10 After completing hydrogen reduction, hydrogen flow is terminated and inert gas flow is continued to purge hydrogen so that oxygen required in the next step can be safely introduced. The purge can be done over a wide range of conditions; for example, passing inert gas through the catalyst at about atmospheric to about
15 2.07 MPaa (300 psia) and about 450°C to about 550°C, preferably between about 450°C to about 530°C, above about 15.2 cm/sec (0.5 FPS) for about 30 minutes adequately clears hydrogen.

This Sheet Has Been Replaced



TABLE 1
RANGES OF CONDITIONS

	<u>Components</u>	<u>Suitable</u>	<u>Preferable</u>	<u>More Preferable</u>	<u>Most Preferable</u>
Primary Coke Burn (a1)	Oxygen Water Pressure Temperature	500-6000 ppm 0-1.5 psia 14.7-300 psia 400-500°C	1000-4000 ppm 0-0.75 psia 14.7-200 psia 400-480°C	0-0.1 psia 50-200 psia 400-450°C	
Secondary Coke Burn (a2)	Oxygen Water Pressure Time End Point Temperature	up to 10 psia up to 1.5 psia 14.7-300 psia >6 hours CO ₂ <0.01 psia 510°C	0.1-5 psia up to 0.75 psia 14.7-200 psia 36-80 hours CO ₂ <0.004 psia 520-600°C	2-4 psia 0.2-0.75 psia 50-200 psia 48-75 hours 530-550°C	0.2-5 psia 60-75 hours 530-540°C
Oxychlorination (b)	Oxygen Water Chlorine Source of Cl Pressure Temperature Breakthrough	up to 10 psia up to 1.5 psia >0.03 psia Chlorohydrocarbons HCl and Cl ₂ >14.7 psia 480-550°C HCl or Cl ₂ >0.02 psia	1-5 psia up to 0.75 psia 0.03-3 psia HCl, Cl ₂ , and CCl ₄ 14.7-300 psia 500-530°C	2-4 psia 0.2-0.75 psia 0.05-1 psia HCl and Cl ₂ 50-200 psia about 510°C	0.2-0.5 psia 0.1-0.5 psia Cl ₂
Stripping (c)	Oxygen Water Pressure Temperature End Point	<4.5 psia up to 1.5 psia 14.7-65 psia >450°C HCl<0.004 psia	<3 psia 0-0.75 psia 14.7 psia 450-530°C HCl<0.003 psia	0.7-3 psia 0-0.04 psia 480-520°C HCl<0.00155 psia	0.05-0.4 psia about 510°C
Reduction (d)	Hydrogen Water Pressure Temperature HCl Release	>0.015 psia 0-1.5 psia 14.7-65 psia >450 °C <0.0075 psia	0.015-14.7 psia up to 0.75 psia 14.7 psia 450-530°C	0.15-5 psia 0-0.4 psia 480-520°C	0.4-1 psia 0.05-0.4 psia about 510°C
Option Reduction After coke burn (a')	Hydrogen Water Pressure Temperature	>0.015 psia 0-1.5 psia 14.7-300 psia 300-500°C	0.015-14.7 psia 0-0.75 psia 14.7-200 psia 450-530°C	0.15-5 psia 0.2-0.75 psia 14.7-65 psia 480-520°C	0.4-1 psia 0.2-0.5 psia 14.7 psia



The regeneration procedure of the present invention is particularly effective for regenerating severely deactivated catalysts which are not fully regenerated using known procedures. Also, the present procedure regenerates normally deactivated catalyst to higher activity and selectivity than known procedures.

The effluent gas, i.e., the gas stream from the outlet of the vessel containing the catalyst, can be recycled. If it is recycled then a fraction of the effluent gas must be purged and replaced with fresh inert gas. The purge rate is typically 5% to 30% of the recycle gas rate.

For purposes of the present invention, preferred catalysts are monofunctional catalysts based on large pore zeolite crystals bound together by a binder which is preferably kaolin, silica, or most preferably alumina. The large pore zeolite is preferably zeolite L and more preferably includes exchangeable cations at least a portion of which are selected from lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, and mixtures of any two or more thereof. More preferably the exchangeable cation is potassium or barium, and most preferably potassium.

The Group VIII catalytic metals are preferably noble metals e.g., platinum, palladium, rhodium, iridium, ruthenium and osmium, and most preferably platinum. The amount of the Group VIII catalytic metal present is preferably from 0.05% to 6% by weight.

The catalytic metal may further comprise a Group VII B metal, such as rhenium. The Groups identified herein are as presented in the Periodic Table in the Handbook of Chemistry & Physics, published by the Chemical Rubber Company, 48th edition.

In a preferred embodiment, the base of the



catalyst is approximately 70% zeolite L and 30% alumina by weight and is formed into 0.16 cm extrudates. For purposes of the present invention, however, binders other than alumina, such as silica, kaolin and clay may be used; and formed shapes, other than extrudates, such as spheres, tablets, pellets and extrudates may also be used. The formed catalyst is preferably loaded with platinum by ion exchange so that the metal loading is preferably between 0.6% and 0.9% by weight.

Representative publications disclosing details of catalyst preparation, characterization, and manufacture include US-A-3,216,789 which describes zeolite L; US-A-4,104,320; 4,416,806; and, 4,568,656 which describe processes of ion exchange of platinum into zeolite L; and US-A-4,595,668; 4,595,669; and 4,595,670 which describe preferred reforming catalysts comprising platinum on zeolite L which has finely dispersed platinum.

The activity of a catalyst is a measure of its ability to convert feed to products. While a catalyst may have a high activity, the products formed may not be necessarily the desired products. The term "selectivity" is a measure of the ability of the catalyst to convert feed to desired products. Activity maintenance concerns the ability of the catalyst to maintain activity over time at conversion conditions.

The decline in catalyst activity at conversion conditions is believed to be due primarily to crystal growth or agglomeration of the noble metal particles to about the size of the zeolite channels (about 12Å) and secondarily to the formation of coke on the external and internal surfaces of the catalyst. At the same noble metal loading, catalysts containing particles or crystals of noble metals of a size greater than that disclosed above are less active and less selective than

This Sheet Has Been Replaced



catalysts containing the smaller particles. Moreover, agglomerated metal particles block zeolite channels. Coke formation, probably due to complex condensation and dehydrogenation reactions, results in the shielding of the noble metal from the reaction mixture, thereby limiting the catalytic sites available for promoting reactions.

As catalytic activity declines by virtue of agglomeration and coke formation, yield of desirable products will decline, and depending upon the economics of the operation a process employing the catalyst will have to be interrupted and catalyst activity restored to its initial value. Generally, catalytic activity can be maintained by increasing temperature, but there are limits beyond which the temperature cannot be increased, for example, temperatures which will change the nature of the zeolite or lead to undesirable side reactions or exceed reactor material limitations. Particularly for zeolite based catalysts, temperatures higher than 538°C or 594°C (1000°F or 1100°F) are preferably avoided.

Catalyst activity will decline faster over time as severity increases. Factors which increase severity include: increasing temperature, reducing hydrogen to oil mole ratio, reducing hydrogen partial pressure, reducing total pressure and temperature, increasing feed rate per volume of catalyst (space velocity), and increasing type of hydrocarbon in the feed.

In the measurement of activity maintenance all variables are fixed and only the catalyst differs. Thus, an activity of one catalyst over a period of time can be directly compared to the activity of another catalyst over the same time period where feed, hydrogen to oil ratios, pressures, etc., are constant.

One activity test utilized for purposes of the



present application is to pass a feedstream comprising about 40 wt. % normal hexane and 60% isohexanes over the catalyst at the following conditions: 510°C, 1.0 weight hourly space velocity (WHSV), 839 kPaa (121.7 psia), 4.25 H₂/oil molar ratio. Benzene yield as a percent of feed after 46 hours is a good measure of catalyst activity.

Although the regeneration process herein may apply to deactivated catalysts at any stage of deactivation, it is particularly suitable for those which are severely deactivated.

This Sheet Has Been Replaced



EXAMPLES

The following examples illustrate the invention. In all examples, parts and percentages are given by weight for solids and liquids and by volume for gas compositions, and temperatures in degrees Centigrade unless otherwise noted. Examples 1 through 18 were performed at one atmospheric total pressure. In all Examples, the HCl level in the effluent gas after the stripping step (c) and after the reduction step (d) was less than 27.6 Paa (0.004 psia) and in most cases less than 2.76 Paa (0.0004 psia) partial pressure, as measured or calculated.

Example 1

A 0.64 wt % Pt on KL-zeolite extruded catalyst was used to aromatize a light naphtha feed. The flow of hydrogen to the reactor was cut off and the catalyst was exposed to pure hydrocarbon feed for about 5 hours at reforming conditions. The catalyst was thus deactivated, i.e., coked up severely, as indicated by accumulation of about 15 wt. % by weight of coke in contrast to a normally deactivated catalyst which typically contains about 1 wt. % coke.

Two grams of the severely deactivated catalyst were regenerated by the following standard HCl + O₂ redispersion procedure:

First coke deposit was removed by burning (a1) at 450°C with 20 vol. % O₂ in helium at 500 cc/min. for 30 minutes; then temperature was increased to 510°C and water at 2.2 vol. % was added, and the catalyst was subjected to these conditions (a2) for 2 hours. Next HCl was added to the gas stream to give 0.16 vol. % and at the same time oxygen concentration was reduced to 10 vol. %, resulting in a low approaching zero Cl₂ partial



pressure. The total gas flow rate was maintained at 500 cc/min. The oxychlorination treatment (b) was performed for 2.5 hours with a breakthrough HCl + Cl₂ partial pressure of 16.6 kPaa (2.4 psia). After the
5 previously described oxychlorination procedure, the catalyst was treated (c) with 2.2 vol. % water, 10 vol. % O₂ and 87.8 vol. % helium for 1 hour. Oxygen was purged out in about 10 minutes with wet helium containing about 2% water vol. %. Hydrogen reduction
10 (d) was conducted at 510°C with 10 vol. % H₂, and 2.2 vol. % H₂O and 87.8 vol. % helium at a flow rate of 500 cc/min. for 1.5 hours. The regenerated catalyst was designated as Catalyst A.

15

Example 2

The coked catalyst used in Example 1 was regenerated with the regeneration procedure as described in Example 1 except that during the second stage (a2) of the coke burn procedure, the temperature
20 was increased to about 530°C which was thereafter employed and the treat time was extended to about 6 hours; also during oxychlorination, 0.82 vol% Cl₂ instead of HCl was employed, [Cl₂ partial pressure and breakthrough HCl and Cl₂ partial press each approx. 834
25 Paa (0.121 psia)]. The regenerated catalyst regenerated in accordance with the present invention was designated as Catalyst B.

Example 3

30 The above two catalysts were evaluated using 3-methylpentane feed. The reaction was carried out at 510°C at a space velocity of 20 w/w/hr, H₂/oil-6 (6 molar ratio of H₂ to oil), and 724 Paa (105 psia). Table 2 shows the catalyst performance of Catalyst A
35 and B. Catalyst B which was regenerated by a process



in accordance with the present invention shows a higher benzene yield and selectivity than Catalyst A.

Table 2

5

<u>Catalyst</u>	<u>Wt% Benzene</u>	<u>Wt% Benzene</u>	<u>Selectivity</u>
	<u>@ 10 Hr.</u>	<u>@ 25 Hr.</u>	<u>@ 25 Hr.</u>
A	24.5	20.2	67.3
B	26.3	22.6	68.8

Example 4

A 0.85 wt % Pt on KL-zeolite catalyst was deactivated during aromatization of a light naphtha feed. One gram of this catalyst was regenerated with the procedure of Example 1, except that after the second coke burn, the catalyst was reduced a' at 510°C with 20 vol. % H₂ and 2.2 vol. % water for 1 hour before an HCl + O₂ oxychlorination. The HCl concentration was 0.32 vol. %, (breakthrough partial pressure approx. 324 Paa (0.047 psia); Cl₂ partial pressure approx. zero). The regenerated catalyst was designated as Catalyst C.

20

Example 5

The coked catalyst used in Example 4 was regenerated with the same procedure as Example 2 except that in the second coke burn, the burn time was increased to 22 hours and there was a wet hydrogen reduction (a') before the Cl₂ + O₂ oxychlorination, (Cl₂ and breakthrough partial pressure (pp) as reported in Example 2). The regenerated catalyst was designated as Catalyst D.

30



Example 6

The above two catalysts were evaluated using 3-methylpentane feed. The reaction was carried out at 510°C at a space velocity of 20 w/w/hr, H₂/oil-6, and 724 Paa (105 psia). Table 3 shows the catalyst performance of Catalyst C and D. Catalyst D which was regenerated by the instant invention shows better catalyst performance than Catalyst C.

Table 3

<u>Catalyst</u>	<u>Wt% Benzene</u> <u>@ 10 Hr</u>	<u>Wt% Benzene</u> <u>@ 25 Hr</u>	<u>Selectivity</u> <u>@ 25 Hr</u>
C	22.2	18.3	69.6
D	25.2	20.8	69.8

Example 7

A catalyst was deactivated through 6 cycles of on-oil and regeneration operations in the Catalyst Treating Unit. One gram of this catalyst was regenerated using exactly the same procedure as Example 1 (Cl₂ and breakthrough pp as in Example 1). The regenerated catalyst was designated as Catalyst E.

Example 8

The deactivated catalyst used in Example 7 was employed in this example. Four grams of this catalyst was regenerated using exactly the same procedure as Example 2 except that the time of the coke burn step was extended to 69 hours (Cl₂ and breakthrough pp as in Example 2). The regenerated catalyst was designated as Catalyst F.



Example 9

The above two catalysts were evaluated using 3-methylpentane feed. The reaction was carried out at 510°C at a space velocity of 20 w/w/hr, H₂/oil-6, and 724 Paa (105 psia). Table 4 shows the catalyst performance of Catalyst E and F. Catalyst F which was regenerated by the instant invention shows a better catalyst performance than Catalyst E.

Table 4

<u>Catalyst</u>	<u>Wt% Benzene</u>	<u>Wt% Benzene</u>	<u>Selectivity</u>
	<u>@ 10 Hr</u>	<u>@ 25 Hr</u>	<u>@ 25 Hr</u>
E	19.6	16.0	67.6
F	21.5	18.8	64.6

Advantages of the present invention in the regeneration of Pt on KL-zeolite include the externalization of the Pt particles to the outside surface of the zeolite crystallites during high temperature coke burn which appears to open up the zeolite channels for Pt redistribution in the oxychlorination step. The redispersion of large Pt particles which are larger than about 200 Å requires high concentration of chlorine to facilitate the formation of mobile Pt chloride species. Although not wishing to be bound by any particular theory, it is believed that this redistribution of external Pt into zeolite channels may promote highly dispersed Pt clusters which reside near the channel mouths thereby yielding better catalyst performance.

The following examples using fresh catalysts give

This Sheet Has Been Replaced



some support to the above interpretation.

Example 10

A sample of about 3 grams of a 0.85 wt % Pt/KL-
5 zeolite catalyst was subjected to a 510°C calcination
of 20 vol. % O₂, 2.2 vol. % H₂O and 77.8 vol. % helium
at a flow rate of 500 cc/min. for 2 hours. Less than
10% of the Pt formed particles had a size greater than
10 about 200 Å. Substantial amount of Pt remained inside
the zeolite channels as large and small particles.
This catalyst was designated at Catalyst G.

Example 11

Ten grams of the fresh catalyst used in Example 11
15 were calcined at 530°C in 20 vol. % O₂, 2.2 vol. % H₂O,
and 77.8 vol. % helium at a flow rate of 500 cc/min.
for 64 hours. Substantially all the Pt was removed
from the zeolite channels to the external surface of
the zeolite crystallites as particles larger than about
20 200 Å. This catalyst was designated as Catalyst H.

Example 12

Two grams each of Catalysts G and H were
regenerated using the same regeneration procedure as
25 that in Example 1 except that in oxychlorination higher
HCl concentration (0.58 vol. %) was used, [breakthrough
pp approx. 586 Paa (0.085 psia); Cl₂ pp approx. zero].
The regenerated catalysts were designated as Catalysts
I and J, respectively.

30

Example 13

Two grams each of Catalyst G and H were regenerated
using the same procedure as in Example 12 except that
HCl concentration in oxychlorination was increased to
35 1.08 vol. %, [breakthrough pp approx. 1.1 kPaa (0.159



psia); Cl₂ pp approx. zero]. The regenerated catalysts were designated as Catalysts K and L respectively. Catalysts I, J, K, and L were evaluated by 3-methylpentane aromatization and hydrogen chemisorption as described in Example 3. The results are in Table 5. Higher concentrations of HCl produces higher Cl₂ concentration via the Deacon reaction:



10

Table 5

<u>Catalyst</u>	<u>H/Pt</u>	<u>Wt% Benzene</u> <u>@ 25 Hr</u>	<u>Bz Selectivity</u> <u>@ 25 Hr</u>
Fresh	0.78	19.4	68.2
I	0.59	22.2	67.6
J	0.37	18.6	68.7
K	0.71	22.9	69.3
L	0.59	21.2	68.5

Table 5 indicates that higher HCl concentration in the HCl + O₂ oxychlorination improves platinum dispersion for the 510°C calcined catalysts (Catalysts I and K) from 0.59 to 0.71 and 530°C calcined catalysts (Catalysts J and L) from 0.37 to 0.59. Catalyst performance is also affected, especially in the case of catalysts J and L.

20

Example 14

Two grams each of Catalysts G and H were regenerated using the same regeneration procedure as that in Example 2 in which oxychlorination was carried out with 0.82 vol. % Cl₂ [breakthrough and Cl₂ pp as in Example 2]. The regenerated catalysts were designated as Catalysts M and N respectively. Catalysts M and N

25

This Sheet Has Been Replaced



were evaluated by 3-methylpentane aromatization and hydrogen chemisorption [as in Example 3]. The results are in Table 6.

5

Table 6

<u>Catalyst</u>	<u>H/Pt</u>	<u>Wt% Benzene</u> <u>@25 Hr</u>	<u>Bz Selectivity</u> <u>@25 Hr</u>
Fresh	0.78	19.4	68.2
M	0.73	21	69.8
N	0.74	25.4	70.2

Table 6 indicates that high Cl₂ concentration completely redisperses the particles of Pt which are 200 Å formed during the 530°C calcination. Additionally, the 530°C calcined catalyst (N) showed a much higher activity than the fresh and the 510°C calcined catalyst (M) after Cl₂ + O₂ oxychlorination. Although not wishing to be bound by any particular theory, this suggests that redispersion of the large Pt particles on the external surface of the zeolite crystallites (530°C calcined catalyst (N)) leads to highly dispersed Pt clusters in the zeolite channels but close to the channel mouths compared to the case of redispersing agglomerated Pt particles inside zeolite channels (510°C calcined catalyst (M)).

Example 15

A 0.84 wt % Pt on KL-zeolite extruded catalyst was used to aromatize a light naphtha feed. The catalyst was severely deactivated and heavily coked. The color of the catalyst was black. Three grams of the catalyst were regenerated by the following HCl + O₂ redispersion procedure. First coke deposit was removed by burning



at 450°C with 10 vol. % O₂ in helium at 1000 cc/min. for 1 hour. Then temperature was increased to 510°C and held at 510°C for 12 hours. Next water and HCl were added to the gas stream to give 3.3 vol. % water and 0.33 vol. % HCl, and at the same time oxygen concentration was still maintained at 10 vol. %. The total gas flow rate was maintained at 1000 cc/min. The oxychlorination treatment (b) was for 6 hours; [breakthrough pp 338 Paa (0.049 psia); Cl₂ pp approx. zero]. The catalyst was then cooled to 345°C under substantially same gas environment and was treated with 3.3 vol. % water, 10 vol. % O₂ and 87.8 vol. % nitrogen for 1 hour. Oxygen was purged out in about 10 minutes with nitrogen. Hydrogen reduction was conducted at 345 °C with 10 vol. % H₂ and 90 vol. % helium at a flow rate of 1000 cc/min for 1 hours. The regenerated catalyst was designated as Catalyst O.

Example 16

The coked catalyst used in Example 15 was regenerated with the regeneration procedure in accordance with the present invention. The coke was first removed by burning (a1) at 445°C with 10 vol. % oxygen in nitrogen for 1 hour. The temperature was raised to 530°C under 20% O₂, 2.2% H₂ and balanced helium. The catalyst temperature was held (a2) at 530° C for 69 hours before it was cooled to 510°C. During oxychlorination (b), catalyst was treated with a gas mixture of 2.2%H₂O, 20%O₂, 1.5% Cl₂, and balanced He for 2.5 hours at 510°C, [Cl₂ and breakthrough pp = 15.2 kPaa (0.221 psia)]. After the oxychlorination, the catalyst was treated (c) with 2.2 vol. % water, 10 vol. % O₂, and 87.8 vol. % helium at 510°C for 1 hour. Oxygen was purged in about 10 minutes with wet helium. Hydrogen reduction (d) was conducted at 510°C with 20%



H₂, 2.2 vol.% water and 87.8 vol. % helium at a flow rate of 500 cc/min. for 1.5 hours. The regenerated catalyst was designated Catalyst P.

5

Example 17

Catalysts O and P and fresh catalyst were evaluated by an aromatization reaction with a mixed feed of 60 wt% 3-methyl pentane and 40 wt% n-hexane. The reaction was carried out at 510°C at a space velocity of 8 w/w/hr, H₂/oil-2.5, and 724 Paa (107 psia). Table 7 shows the catalyst performance of fresh catalyst and Catalysts O and P. Catalyst P which was regenerated by the current invention shows a better catalyst performance than Catalyst O and fresh catalyst.

15

Table 7

<u>Catalyst</u>	<u>Wt% Benzene</u> <u>@ 46 Hr</u>	<u>Bz Selectivity</u> <u>@ 46 Hr</u>
Fresh	37	76
O	33	65
P	40	75

Example 18

A 0.85 wt% Pt on KL-zeolite catalyst was used to aromatize a light naphtha feed. The catalyst was normally deactivated in that it contained about 1-2% coke. The coke level was regenerated by the conventional procedure as described in Example 15. This catalyst is designated as Catalyst Q.

25

In parallel, three grams of the catalyst were regenerated by the regeneration procedure in accordance with the present invention as described in Example 16. This catalyst is designated as Catalyst R. Catalysts Q



and R were evaluated under the aromatization test condition described in Example 17. Table 8 indicates that the regeneration procedure in accordance with the present invention achieves higher activity and selectivity than a conventional procedure used to regenerate a normally deactivated catalyst.

Table 8

<u>Catalyst</u>	<u>Wt% Benzene</u> <u>@ 46 Hr</u>	<u>Bz Selectivity</u> <u>@ 46 Hr</u>
Q	37	72
R	40	75

Example 19

A 0.85 % wt. % Pt on formed KL-zeolite catalyst was used to aromatize a light naphtha feed. The catalyst was normally deactivated, i.e., the catalyst contained about 1-2% coke. The catalyst was regenerated using the following procedure:

The coke was removed by coke burn (a1) at 450°C for 10 hours with 0.2 vol. % oxygen in nitrogen under 1.28 MPaa (185 psia) total pressure and 15.2 cm/sec (0.5 FPS) linear velocity. The coke burn (a2) was further carried out at 510°C for 16 hours with 3.5 vol. % oxygen. After oxygen was purged out, the catalyst was reduced (a') at 510°C with 50% hydrogen for 1 hour. After hydrogen was purged out, the catalyst was then pre-conditioned for oxychlorination with 0.89 vol. % oxygen and 0.87 vol. % water vapor at 510°C under 1.17 MPaa (170 psia) total pressure. HCl was added to the stream to a concentration of 0.15 vol. % for 4.5 hours [breakthrough pp = 889 Paa (0.129 psia); Cl₂ pp 69 Paa (0.010 psia)]. The catalyst was cooled to 345°C under



same gas environment. The catalyst was then treated with 5 vol. % oxygen and 0.84% vol. % water vapor at 345°C under atmospheric pressure for 8 hours. Water vapor was removed from the stream, and the catalyst was further treated at 345°C for 2 hours. After oxygen was purged out from the system, the catalyst was reduced at 345°C with 7 vol. % hydrogen for 6 hours. The catalyst is designated as Catalyst S.

A batch of the similar normally deactivated 0.85% Pt/KL-zeolite catalyst was regenerated by a regeneration procedure in accordance with the present invention. The coke was removed by coke burn (a1) at 450°C for 10 hours with 0.2 vol% oxygen in nitrogen under 1.17 MPaa (185 psia) total pressure and 15.2 cm/sec (0.5 FPS) velocity. The coke burn was further carried out (a2) at 530°C for 69 hours with 1.6 vol. % oxygen and 0.2 vol. % water vapor. The catalyst was oxychlorinated (d) with 1.7 vol. % oxygen, 0.12 vol. % Cl₂, and 0.2 vol. % H₂O at 510°C for 2.5 hours under 1.17 MPaa (185 psia) total pressure, [breakthrough pp = 2.04 kPaa (0.296 psia); Cl₂ pp = 1.53 kPaa (0.222 psia)]. The catalyst was then treated (c) with 10.5 vol. % oxygen and 2.2 vol. % water vapor at 510°C under atmospheric pressure for 10 hours; to an HCl partial pressure of 45.5 Paa (0.0066 psia). After oxygen was purged out from the system, the catalyst was reduced (d) at 510°C with 5.8 vol. % hydrogen and 2.2 vol. % water vapor for 1.5 hours at atmospheric pressure, to an HCl pp of 15.2 Paa (0.0022 psia). The catalyst is designated as Catalyst T.

The activities of Catalysts S and T in light naphtha aromatization under the following conditions:



	<u>Feedstream</u>	<u>Conditions</u>
	Mixed C ₆ s	1.8 WHSV
5	60% nC ₆	2 H ₂ /Oil Molar Ratio
	40% iC ₆	105 psia
		505°C

The normally deactivated catalyst regenerated in accordance with the present invention has higher activity and selectivity than the catalyst regenerated by the HCl procedure.

Table 9

<u>Catalyst</u>	<u>Wt% Benzene</u> <u>@ 100 Hr</u>	<u>Bz Selectivity</u> <u>@ 100 Hr</u>
S	43	66
T	48	68

15

The catalysts regenerated by the process of this invention may be employed as reforming catalysts using reforming conditions which are well known in the art.

In summary, the present invention is seen to provide a method which is particularly effective for regenerating severely deactivated reforming catalysts, preferably extrudates of potassium-exchanged zeolite L containing platinum, so as to substantially restore catalyst activity and activity maintenance to the catalyst. The regeneration procedure of the present invention, however, is also useful for regenerating normal deactivated reforming catalysts.



CLAIMS:

1. A process for regenerating a deactivated catalyst comprising a Group VIII catalytic metal and zeolite, which process comprises:

5 a) contacting the deactivated catalyst with a gaseous stream comprising oxygen, inert gas and water under oxidation conditions comprising a temperature of from 400°C to 600°C for a time sufficient to burn coke
10 off the deactivated catalyst and convert the metal to agglomerated particles which are accessible to chlorine-containing gas in subsequent process step (b), to result in a substantially decoked catalyst;

b) contacting the substantially decoked
15 catalyst with a gaseous stream comprising water, a source of chlorine, oxygen and an inert gas under oxychlorination conditions comprising a temperature of from 450°C to 550°C and a partial pressure of chlorine derived from the source of chlorine which is greater
20 than 207 Paa (0.03 psia) for a time sufficient for hydrogen chloride and/or chlorine to breakthrough the catalyst to an HCl + Cl₂ partial pressure greater than 138 Paa (0.02 psia) so as to chlorinate and disperse the metal and result in a chlorinated catalyst
25 comprising substantially completely dispersed chlorine-complexed metal;

c) contacting the chlorinated catalyst with a gaseous stream comprising water, oxygen, and an inert gas under chlorine removal conditions comprising a
30 temperature of from 450°C to 550°C, a low total pressure, and a time effective to remove from the chlorinated catalyst at least some of the chloride complexed to the metal and result in a gaseous stream after contact with the catalyst comprising hydrogen
35 chloride at a partial pressure of less than 27.6 Paa





(0.004 psia); and

d) contacting the chlorinated catalyst from step (c) with a gaseous stream comprising inert gas and hydrogen under reducing conditions comprising a low total pressure and a temperature of from 350°C to 550°C for a time effective to reduce at least some of the chlorine- complexed metal in the catalyst to the metallic state and result in a regenerated catalyst comprising dispersed metal and zeolite.

10

2. A process according to claim 1 wherein step (a) is performed at a temperature of from 520°C to 600° C and/or at an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or at a water partial pressure not greater than 10.3 kPaa (1.5 psia) and/or at a total pressure of from sub-atmospheric to 2.07 MPaa (300 psia) and/or for a time of from 48 to 75 hours.

15

3. A process according to claim 1 or 2 wherein step (a) is performed for a period of time until the gaseous stream after contact with the catalyst comprises a partial pressure of carbon dioxide of less than 69 Paa (0.01 psia), preferably less than 27.6 Paa (0.004 psia).

25

4. A process according to any preceding claim in which step (a) is performed in a first stage (a1) and a second stage (a2) wherein stage (a1) is performed at a lower temperature than stage (a2).

30

5. A process according to claim 4 wherein (a1) is performed at a temperature of from 400° to 500°C and (a2) is performed at a temperature of from 520° to 600° C.

35



* C L M S *



6. A process according to any preceding claim wherein step (a) oxidation is carried out until the metal is agglomerated to particles greater than 200 Angstrom in size, a substantial proportion of which are located outside the channels of the zeolite.

7. A process according to any preceding claim wherein step (b) is performed at a temperature of from 480° to 550°C and/or at an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or at a water partial pressure not greater than 10.3 kPaa (1.5 psia) and/or at a total pressure of from sub-atmospheric to 2.07 MPaa (300 psia) and/or for at least 2 hours after HCl and/or Cl₂ breakthrough.

15

8. A process according to claim 7 wherein step (b) is performed at an oxygen partial pressure of from 13.8 to 27.6 kPaa (2 to 4 psia) and/or at a water partial pressure of from 1.38 to 5.17 kPaa (0.2 to 0.75 psia) and/or at a total pressure of from 345 kPaa to 1.38 MPaa (50 to 200 psia).

9. A process according to any preceding claim wherein step (b) is performed at a chlorine partial pressure of from 207 Paa to 20.7 kPaa (0.03 to 3 psia), preferably from 345 Paa to 6.9 kPaa (0.05 to 1 psia).

10. A process according to any preceding claim wherein step (c) is performed at a temperature of from 480° to 520°C and/or at a water partial pressure not greater than 10.3 kPaa (1.5 psia) and/or at an oxygen partial pressure of less than 31 kPaa (4.5 psia).

11. A process according to claim 10 wherein step (c) is performed at a water partial pressure of from





345 Paa to 2.76 kPaa (0.05 - 0.4 psia) and/or at an oxygen partial pressure of from 4.82 Paa to 20.7 kPaa (0.7 to 3 psia).

5 12. A process according to any preceding claim wherein step (c) is performed at a total pressure of from sub-atmospheric to 448 kPaa (65 psia), preferably at about atmospheric pressure.

10 13. A process according to any preceding claim wherein step (c) is performed for a period of time until the gaseous stream after contact with the catalyst comprises a partial pressure of hydrogen chloride of less than 10.3 Paa (0.0015 psia).

15 14. A process according to any preceding claim wherein step (d) is performed at a hydrogen partial pressure greater than 103 Paa (0.015 psia) and/or at a temperature of from 480° to 520°C and/or in the
20 presence of water, preferably at partial pressure not greater than 10.3 kPaa (1.5 psia).

 15. A process according to claim 14 wherein step (d) is performed at a hydrogen partial pressure of from
25 1.03 kPaa to 34.5 kPaa (0.15 to 5 psia) and/or at a water partial pressure of from 345 Paa to 2.76 kPaa (0.05 to 0.4 psia).

 16. A process according to any preceding claim
30 wherein step (d) is performed at a total pressure of from sub-atmospheric to 448 kPaa (65 psia), preferably at about atmospheric pressure.

 17. A process according to any preceding claim
35 wherein step (d) is performed under conditions such





that the gaseous stream after contact with the catalyst comprises hydrogen chloride at a partial pressure of less than 51.7 Paa (0. 0075 psia).

5 18. A process according to any preceding claim wherein between steps (a) and (b) there is performed an intermediate reducing step (a') comprising contacting the substantially decoked catalyst with a gaseous stream comprising inert gas and hydrogen under reducing
10 conditions for a time effective to reduce the metal component of the catalyst to the metallic state.

 19. A process according to any preceding claim wherein between steps (c) and (d) there is performed a
15 purging step (c') comprising contacting the chlorinated catalyst from step (c) with an oxygen-free displacement gas flow for a time sufficient to purge oxygen therefrom prior to performing step (d).

20 20. A process according to any preceding claim wherein the catalyst comprises a type L zeolite optionally containing potassium or barium as exchangeable cations and/or the Group VIII catalytic metal comprises platinum and/or the Group VIII metal is
25 present as from 0.05 to 6 wt% of the catalyst, which optionally comprises a binder.

 21. A process according to any preceding claim wherein the regenerated catalyst produced in step (d)
30 has an activity for aromatizing hexanes to benzene in accordance with the test defined in Example 3 hereof, measured in weight percent yield of benzene, which is at least 1.5 wt% greater than the activity of the low activity catalyst before regeneration according to the
35 invention.



22. A process for reforming hydrocarbons comprising contacting hydrogen and naphtha with a catalyst regenerated in accordance with the process according to any preceding claim, to produce aromatic hydrocarbons.
- 5

This Sheet Has Been Replaced



* C L M S *