

THIS SHEET HAS BEEN
REPLACED

- 1 -

IMPROVED METHOD OF REGENERATING DEACTIVATED CATALYST

1. Field of Invention

5 This invention relates to regenerating deactivated zeolite based catalysts and enhancing the activity of fresh zeolite based catalysts, particularly, but not exclusively, large pore zeolite catalysts such as zeolite L catalysts.

10 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.

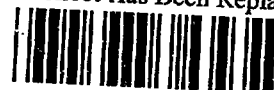
15 Zeolite based reforming catalysts deactivate and periodically must be regenerated to recover activity.

20 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 principal source of aromatic chemicals, i.e., benzene, toluene and xylenes, via conversion of paraffins and naphthenes to aromatics.

25 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 branched paraffins, dealkylation of alkylbenzenes, and hydrocracking of paraffins to light hydrocarbons. The hydrocracking of paraffins to light hydrocarbons is
30 undesirable and should be minimized because light hydrocarbons have low value.

Reforming is typically carried out at temperatures of 426 to 538°C (800 to 1000°F), pressures of 0.34 to 20.7 Mpa (50 to 3000 psi), hourly weight space

This Sheet Has Been Replaced



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

Other characteristics of reforming processes are well known in the art, and reference is made to US-A-4
5 914 068 for further teachings on this topic.

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.
10 Typically, chlorine is incorporated on the alumina to add acid functionality. Alumina-based reforming catalysts are suitable for aromatizing C₈+ paraffins, but are less effective for aromatizing C₆ to C₈ paraffins because these catalysts hydrocrack more of
15 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
20 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
25 been developed which are 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
30 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,
35 undesirable hydrocracking reactions are repressed.



THIS SHEET HAS BEEN
REPLACED

- 3 -

Large pore zeolites are preferred for reforming catalysts, 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
5 zeolite L being the most preferred support for reforming catalysts, particularly wherein the catalytically active metal is platinum.

For commercial reforming processes, zeolite catalysts are preferably formed into aggregates, such
10 as extrudates or tablets, typically 0.08 to 0.65 cm in size to reduce pressure drop.

During reforming, catalysts deactivate due to accumulation of coke deposits in the catalyst, and agglomeration of the fine catalytic metal particles
15 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
20 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, 2) redispersing the active catalytic metals by
25 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 (oxygen post treating), and 4) reducing the dispersed catalytic metal using a reducing agent such
30 as hydrogen.

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

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

FR-A-2,360,540 teaches that catalyst regeneration is improved by subjecting the catalyst after oxychlorination to a treatment with water and cooling air before the catalyst is reduced.

5 US-A-4 925 819 teaches a procedure 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.

EP-A-0 142 352 is similarly directed to the
10 process of regenerating a deactivated catalyst or enhancing the activity of a fresh catalyst and discloses that a wet nitrogen stripping step at temperatures no greater than about 450°C may be performed between the previously mentioned steps of
15 post treating with oxygen and reducing with hydrogen.

US-A-4 914 068 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
20 oxygen before the reduction.

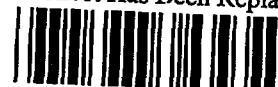
Attention is directed to the above-mentioned US-A-4 925 819, US-A-4 914 068, EP-A-0 142 352 and FR-A-2360540 for extensive teachings on zeolite catalysts, reforming processes and catalyst regeneration
25 techniques, all of which are applicable to performance of the present invention.

SUMMARY OF THE INVENTION

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

(a) contacting the deactivated or low activity catalyst with a gaseous stream comprising inert gas and
35 oxygen under oxidation conditions for a time effective

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 5 -

to burn coke off the deactivated or low activity catalyst to result in a substantially decoked catalyst;

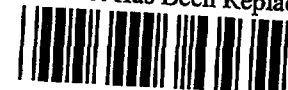
(b) contacting the substantially decoked catalyst with a gaseous stream comprising inert gas, oxygen, water and a source of halogen under oxyhalogenation conditions comprising a temperature of from 450°C to 550°C and a time effective to halogenate and disperse the metal to result in a halogenated catalyst comprising dispersed halogen-complexed metal;

(c) contacting the halogenated catalyst with a gaseous stream comprising inert gas and oxygen under halogen removal conditions comprising a temperature of 300°C to 400°C, a low total pressure and a time effective to remove from the halogenated catalyst at least some of the halogen complexed to the metal and result in a gaseous stream after contact with the catalyst comprising hydrogen halide at a partial pressure of less than 27.6 Paa (0.004 psia); and

(d) contacting the halogenated catalyst from step (c) with a gaseous stream comprising hydrogen and optionally an inert gas, under reducing conditions comprising a low total pressure for a time effective to reduce at least some of the halogen-complexed metal in the catalyst to the metallic state and result in a regenerated catalyst comprising dispersed metal and zeolite and a gas flow after contact with the catalyst comprising hydrogen halide at a partial pressure of less than 51.7 Paa (0.0075 psia).

This invention is distinguished and advantageous over the prior art in several respects. Thus EP-A-0 142 352 teaches a regeneration process wherein the steps corresponding to steps (b) and (c) of the invention are performed at the same temperature ranges. It has been found according to the instant invention that controlling the process conditions, including

This Sheet Has Been Replaced



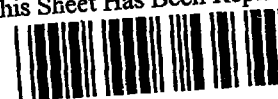
- 6 -

THIS SHEET HAS BEEN
REPLACED

temperature, within certain specified ranges enables regeneration to occur in a commercially acceptable time without substantive damage to the catalyst. Example 1 of EP-A- 0 142 352 teaches that performance of a wet O₂ post-treat step (corresponding to instant step (c)) on the product of an oxyhalogenation step (corresponding to instant step (b)), at 200°C or lower (instead of about 510°C), in accordance with FR-A-2360540, results in a worsening catalyst performance. Thus, EP-A- 0 142 352 teaches away from performance of step (c) at a lower temperature than step (b).

In contrast, US-A-4 914 068 teaches that the performance of a Group VIII metal-containing catalyst, particularly a catalyst including a Group VIII metal on a large pore zeolite substrate such as zeolite L, can be materially improved by cooling the catalyst between the dispersion step (corresponding to instant step (b)) and the reduction step (corresponding to instant step (d)) of an activation or regeneration process while substantially maintaining the dispersion of the Group VIII metal, and conducting at least the initial portion of the reduction step at a relatively low temperature. Such cooling step may be corresponded to instant step (c). US-A-4 914 068 provides an excellent description of many of the aspects of catalyst regeneration which are equally applicable to the present invention. However, this prior art fails to identify or point the person of ordinary skill in the art towards the key parameters in the present invention which constitute surprising effect. These are that in addition to temperature, step (c) process conditions are controlled to a low total pressure e.g. less than 690 kPaa (100 psia), preferably not greater than 448 kPaa (65 psia), e.g., from sub-atmospheric to 448 kPaa (65 psia) and most preferably about atmospheric pressure; and to a

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

- 7 -

partial pressure of hydrogen halide in the gaseous stream after contact with the catalyst, i.e., in the effluent gas, of less than 27.6 Paa (0.004 psia), preferably less than 20.7 Paa (0.003 psia) or 13.8 Paa (0.002 psia), most preferably less than 10.3 Paa (0.0015 psia) and particularly less than 4.8 Paa (0.0007 psia).

US-A-4 914 068 teaches that the effluent gas stream from the step corresponding to instant step (c) should have an HCl concentration of less than about 300 vppm, and desirably still lower (column 13); and is followed by a reduction step corresponding to instant step (d) with an effluent gas stream having an HCl concentration preferably less than about 75 ppmv (column 14). It has now surprisingly been found that the key factor in the regeneration process is not hydrogen halide concentration on completion of step (c) and (d), but rather the hydrogen halide partial pressure. The teachings of US-A-4 914 068 all relate to processes at one atmosphere pressure, at which the preferred 300 vppm level corresponds to a partial pressure of 30.3 Paa (0.0044 psia). However, when the prior art process is performed at the more normal reforming and regeneration pressure range of 1.03 to 1.38 MPaa (150 to 200 psia) the preferred 300 vppm level equates to a hydrogen halide partial pressure of 310 Pa (0.045 psia).

Step (c) of the invention adopts temperature and pressure conditions which will result in the very low hydrogen halide partial pressure required in accordance with the invention, preferably less than 10.3 Paa (0.0015 psia). At these levels the driving force for hydrogen halide desorption, determined by the equilibrium between the metal halogen complex in the catalyst of step (c) and the hydrogen halide vapor, is

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

- 8 -

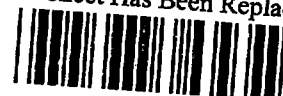
such as to permit dehalogenation in commercially acceptable time periods. The alternative would be to run at normal regeneration pressure, under which condition extremely long periods would be needed to achieve the low hydrogen halide partial pressures, which long periods under regeneration conditions could damage the catalyst.

The halogen removed from the halogenated catalyst in step (c) is that which has become bound directly to the zeolite, and at least some of the halogen complexed to the metal atoms which have become dispersed over the zeolite during oxyhalogenation step (b). Removal of such complexed halogen is believed to fix the metal in dispersed positions. In addition it results in less hydrogen halide release during subsequent reduction, thus helping to reduce re-agglomeration during the reduction step. Here, the relatively low temperature of step (c) contributes to the regeneration efficiency by not promoting re-agglomeration of the metal.

The reduction step (d) of the invention is also performed at low total pressure, e.g. less than 690 kPaa (100 psia), preferably not greater than 448 kPaa (65 psia), e.g. from sub-atmospheric to 448 kPaa (65 psia); so as to result in a hydrogen halide partial pressure in the effluent gaseous stream of less than 51.7 Paa (0.0075 psia). This low value permits hydrogen halide to escape as the metal is reduced, and so minimizes re-agglomeration. Step (d) is preferably performed at a temperature lower than step (b), more preferably from 300 to 400°C. The hydrogen partial pressure employed is preferably greater than 103 Paa (0.015 psia).

Preferably, the catalyst is a formed catalyst, more preferably in the form of tablets, pellets, spheres, and extrudates. The catalyst may include a

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 9 -

binder material, preferably comprising kaolin, alumina, silica or mixtures of any two or more thereof to promote binding into aggregates. As used herein alumina binder materials include, but are not limited to, alkali and alkaline earth - containing alumina. The catalyst most preferably is monofunctional and non-acidic, and the zeolite is a large pore zeolite, which preferably is a type L zeolite. The type L zeolite preferably comprises exchangeable cations such as lithium, sodium, potassium, rubidium, cesium, calcium, barium, or mixtures of any two or more thereof. Potassium and/or barium are particularly preferred.

The Group VIII catalytic metal is preferably a noble metal such as platinum, palladium, rhodium, iridium, ruthenium or osmium, 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 for example a Group VII B metal, preferably rhenium.

As used herein, the Groups are as presented in the Periodic Table in the Handbook of Chemistry & Physics, published by the Chemical Rubber Company, 48th edition.

The process of the present invention preferably comprises a linear gas velocity through the catalyst of at least 15.2 cm/sec (0.5 FPS). As mentioned, 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. In steps (a) and/or (b) the effluent gas, i.e., the gas stream from the outlet of the vessel containing the catalyst, is preferably recycled through the vessel containing the catalyst, rather than operating as a once-through process. In this case a portion of the effluent gas is

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

preferably purged and replaced with fresh inert gas. The purge rate is typically from 5% to 30% of the recycle gas rate, preferably from 10 to 20%.

5 DETAILED DESCRIPTION OF INVENTION

Preferred embodiments of the process of the invention are now discussed, with specific reference by way of example to chlorine as the halogen, and regeneration in the reactor wherein the catalyst has
10 been employed in a hydrocarbon reforming process.

Pre-Regeneration Reactor Purge (Optional)

The first step in the regeneration procedure is to purge hydrocarbons and then purge hydrogen remaining from hydrocarbon processing out of the reactor. This
15 is done by establishing a flow of hydrogen to the reactor and continuing hydrogen flow until hydrocarbon is displaced by hydrogen. Then hydrogen flow is terminated, and a gas flow comprising inert gas, preferably nitrogen, is established through the
20 catalyst bed and continued until hydrogen is displaced with inert gas. The gas flow is preferably substantially free of contaminants, such as ethylene, CO, and sulfur, and other substances which would be harmful or adversely affect the catalyst. The reactor
25 may be purged in a similar manner between any of the subsequently described steps, to remove any gases from the reactor which might undergo a detrimental or adverse reaction if permitted to remain in the reactor during a subsequent step, such as oxygen and hydrogen.

Purging can be done over a wide range of
30 conditions. Suitable pressures are from 101 kPaa (14.7 psia) to 2.07 MPaa (300 psia), preferably one atmosphere, and suitable temperatures are from 400°C to 500°C. The inert gas flow rate is preferably at least
35 15.2 cm/sec (0.5 FPS) linear gas velocity through the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

- 11 -

catalyst bed at operating pressure and temperature. This insures uniform gas flow distribution across the catalyst bed and effective gas/solid contacting for good purging action. Purging at these conditions for one to five hours adequately purges the reactor. The effluent gas, i.e., the gas stream from the outlet of the vessel containing the catalyst, may be recycled through the vessel containing the catalyst, rather than operating as a once-through process. In this case from 5 to 30% of the recycle gas is replaced with fresh inert gas.

Coke Burn (Step (a) of Invention)

Coke which accumulates on the catalyst during hydrocarbon processing must be removed to regenerate the catalyst because catalytic performance of the regenerated catalyst is impaired if coke residues remain on the catalyst. Coke is removed by burning it off with oxygen, which term includes ozone which speeds up the coke burn. The partial pressure of oxygen in this gas stream during coke burn is preferably up to 69 kPaa (10 psia). However, care must be exercised to avoid exposing the catalyst to excessively high temperatures. Temperatures of from 400 to 550°C are preferably used. In another embodiment, halogen, such as HCl, can be included in this gas flow. The use of HCl during coke burn can effectively remove the carbonaceous residues from the spent catalyst. This procedure dramatically reduces the coke burn temperature and minimizes the problems of local hot spots, the temperature run away, and the metal agglomeration. The coke burn is preferably conducted in two stages: a primary coke burn (a1) at less severe conditions followed by a secondary coke burn (a2) at more severe conditions. Thus, step (a) is preferably performed in a first stage (a1) and a second stage

This Sheet Has Been Replaced

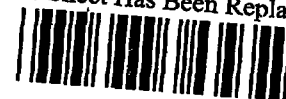


THIS SHEET HAS BEEN REPLACED

(a2), wherein (i) stage (a1) is performed at a lower temperature than stage (a2) and/or (ii) the gaseous stream of stage (a1) has a lower oxygen concentration than that of stage (a2), preferably where (a2) is performed for a longer time than (a1). The two-stage coke burn has been discovered to be advantageous in mitigating risk of exceeding zeolite decomposition temperature at the flame front. The coke burn is preferably conducted at a pressure of from sub-atmospheric to 2.07 MPaa (300 psia) or 1.38 MPaa (200 psia), with a pressure of 345 kPaa (50 psia) to 1.38 MPaa (200 psia), e.g., 1.28 MPaa (185 psia) being more preferred. Gas flow rate to the reactor is preferably set to maintain at least 15.2 cm/sec (0.5 FPS) linear gas velocity through the catalyst.

The primary coke burn is initiated by injecting oxygen, ozone, or air into the inert gas flowing to the reactors. The inlet gas temperature is preferably from 400°C to 500°C, more preferably from 400°C to 480°C, and most preferably about 445°C. The oxygen concentration in the reactor inlet gas is preferably adjusted to from 500 vppm to 6000 vppm, more preferably from 1000 vppm to 4000 ppm. A low concentration of oxygen 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 total pressure. Higher oxygen concentration can be used in the 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 than nitrogen is used. During the primary coke burn the gas flow may be essentially devoid of water or include an amount of water, e.g., to a water

This Sheet Has Been Replaced

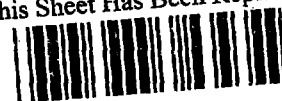


THIS SHEET HAS BEEN REPLACED

partial pressure of up to 20.7 kPaa (3 psia). Thus, the gas stream during coke burn preferably has a partial pressure of water of 0 to 20.7 kPaa (3 psia), more preferably of 0 to 13.8 kPaa (2 psia), and most preferably of 0 to 6.9 kPaa (1 psia). At these conditions the temperature of the catalyst is maintained safely below catalyst decomposition temperature at a most preferred pressure of about 1.28 MPaa (185 psia). CO₂ and oxygen concentration in the reactor outlet gas stream are continuously measured to determine when the primary coke burn is completed, i.e., when molar ratio of CO₂ to O₂ falls below a preferred threshold ratio of 3:1, which occurs typically about two to fifty hours into the burn. The time to complete the primary coke burn step varies with the concentration of coke on catalyst, space velocity, and oxygen concentration in the reactor inlet gas.

Then transition into the secondary coke burn step (a2) is begun. Gas inlet temperature is preferably raised at a rate of about 25 to 50 degrees C per hour to the secondary coke burn temperature which is preferably from 500°C to 550°C, more preferably from 500°C to 520°C, and most preferably at about 510°C, at a most preferred pressure of 1.28 MPaa (185 psia). Simultaneously, oxygen partial pressure is raised to a preferred secondary coke burn level, e.g., up to 69 kPaa (10 psia), more preferably from 690 Paa (0.1 psia) to 55 kPaa (8 psia), and most preferably from 13.8 kPaa (2 psia) to 48.3 kPaa (7 psia). In the secondary coke burn, water may be present for example at a partial pressure up to 20.7 kPaa (3 psia), preferably up to 13.8 kPaa (2 psia), and more preferably up to 6.9 kPaa (1 psia). However, most preferably the gas flow is essentially devoid of water and has a water partial pressure of 0.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 14 -

The secondary coke burn (or single coke burn, if only one stage is used) is continued until the CO₂ partial pressure in the outlet gas from the reactor falls below a preferred level of 69 kPaa (0.01 psia), and more preferably 27.6 Paa (0.004 psia); this typically occurs about 12 hours into the secondary burn, depending on the amount of catalyst in the reactor. It has been discovered that the activity of regenerated catalyst is impaired if the coke burn is terminated prematurely, i.e., before CO₂ partial pressure falls below 27.6 Paa (0.004 psia) to 69 Paa (0.01 psia).

During coke burn, the gas stream is preferably recycled or recirculated from the tail reactor to the lead reactor, where a series of two or more reactors is used, in order to conserve nitrogen of the inert carrier gas by employing an in-line recycle gas compressor. Preferably, about 10% of the recycle gas flow is purged with the fresh coke burn gas prior to recirculating the stream.

Pre-Oxychlorination Hydrogen Reduction (Optional Step (a'))

Regenerated catalyst activity is higher when the catalyst is exposed to hydrogen after coke burn, but before oxychlorination (b). Thus, in a preferred 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 hydrogen under reducing conditions for a time effective to reduce the metal component of the catalyst to the metallic state. Step (a') is preferably performed at a hydrogen partial pressure greater than 103 Paa (0.015 psia) and/or a temperature of from 300 to 550°C and/or a total pressure not greater than 20.7 MPaa (300 psia) and/or

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

with the additional presence of water in the gaseous stream.

As previously discussed, before hydrogen is introduced, oxygen remaining in the reactor after the coke burn must be purged from the reactor to preclude forming combustible mixtures of hydrogen and oxygen, e.g., by cutting off oxygen flow and continuing nitrogen flow through the reactors, e.g., from 30 minutes to several hours at a temperature of about 510° C and at a pressure of from 101 kPaa (14.7 psia) to 2.07 MPaa (300 psia), to reduce oxygen concentration to a safe level; the nitrogen linear velocity is preferably maintained in the catalyst beds at at least 15.2 cm/sec (0.5 FPS) to achieve adequate gas distribution and gas/solid contacting.

Hydrogen reduction is initiated by starting flow of hydrogen into the nitrogen flowing into the reactors. Conditions for hydrogen reduction step (a') can be varied over a wide range. Hydrogen partial pressure is preferably greater than 103 Paa (0.015 psia), more preferably from 103 Paa (0.015 psia) to 101 kPaa (14.7 psia), most preferably from 1.03 kPaa (0.15 psia) to 34.5 kPaa (5 psia), and particularly between 2.76 kPaa (0.4 psia) and 6.9 kPaa (1 psia). Total pressure is e.g. from 101 kPaa (14.7 psia) to 2.07 MPaa (300 psia), preferably to 1.38 MPaa (200 psia), more preferably to 448 kPaa (65 psia), and most preferably at about one atmosphere. Temperatures of from 300°C to 550°C are satisfactory, with 450°C to 530°C being preferred, 480°C to 520°C being more preferred, and about 510°C most preferred. Linear gas velocity through the catalyst beds should achieve uniform gas distribution and effective gas/solid contacting with the catalyst. In an axial adiabatic reactor the gas flow is preferably at least 15.2 cm/sec (0.5 FPS).

This Sheet Has Been Replaced



Reduction time of up to 5 hrs is normally adequate with 30 minutes to 2 hrs being preferred.

Water can be introduced to the reactor (a'), e.g., inlet gas stream during preoxyhalogenation reduction step to yield water partial pressure of up to 6.9 kPaa (1 psia), 13.8 kPaa (2 psia) or 20.7 kPaa (3 psia), although it is most preferred that the gas stream be essentially devoid of water.

After completing hydrogen reduction step (a'), hydrogen flow is cut off 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 one atmosphere to 2.07 MPaa (300 psia) at a temperature of from 300°C to 550°C at a gas flow rate above 15.2 cm/sec (0.5 FPS) for about 30 minutes to several hours adequately clears hydrogen.

In this hydrogen reduction step (a'), as well as the coke burn step (a), wherein the gas is recycled (except for the amount eg 10% purged), hydrogen can be also recycled. This hydrogen reduction step is most preferably performed in once through manner and at atmospheric pressure.

25 Pre-Oxychlorination Conditioning (Optional Step (a'))

The activity of regenerated catalyst is increased by exposing the catalyst to water and oxygen prior to oxychlorination. Thus, according to a preferred embodiment, between steps (a) and (b) there is performed a catalyst conditioning step (a') comprising contacting the catalyst with a gaseous stream comprising inert gas, oxygen and water under conditions and for a time to saturate the catalyst with water and form a substantially water saturated catalyst. Preferably, the substantially saturated catalyst has a



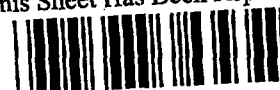
THIS SHEET HAS BEEN
REPLACED

moisture content in equilibrium with the gaseous stream of step (a''). Step (a'') is preferably performed at a temperature of from 300 to 540°C and/or a water partial pressure not greater than 20.7 kPaa (3 psia) and/or an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or a total pressure not greater than 2.07 MPaa (300 psia).

This treatment saturates the catalyst with water and oxidizes metals in the catalyst. The amount of water adsorbed by the oxide support of the catalyst depends on the partial pressure of water in the gas phase. During the reduction step (a'), which is optionally carried out after the coke burn step (a), the amount of water on the catalyst may not be at the right condition since water partial pressure may be too low in the reduction step. The water partial pressure is increased by injecting water into the reactor in the post chlorination conditioning step (a'') so that the oxide support can acquire the equilibrated amount of adsorbed water under the specified water partial pressure. Wetting the catalyst, preferably to saturation prior to initiating oxychlorination avoids exposing dry catalyst to chlorine at oxychlorination conditions which has been discovered to impair activity of regenerated catalyst.

Pre-oxychlorination conditioning step (a'') may be carried out at a pressure of atmospheric to 2.07 MPaa (300 psia), preferably to 1.38 MPaa (200 psia), more preferably of 345 kPaa (50 psia) to 1.38 MPaa (200 psia), and most preferably at about 1.28 MPaa (185 psia), and temperatures of from 300°C to 540°C, with temperatures of 500°C to 530°C being preferred, and a temperature of about 510°C being most preferred. Water partial pressure may be, e.g., up to 20.7 kPaa (3.0 psia), preferably to 13.8 kPaa (2 psia), more

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 18 -

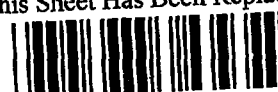
preferably between 1.38 kPaa (0.2 psia) and 13.8 kPaa (2 psia) and most preferably at about 6.9 kPaa (1 psia); oxygen partial pressure may be, e.g., up to 69 kPaa (10 psia), with 69 kPaa (1 psia) to 34.5 kPaa (5 psia) being preferred, and with 6.9 kPaa (1 psia) to 13.8 kPaa (2 psia) being more preferred. Gas linear velocity through the catalyst beds is preferably maintained above 15.2 cm/sec (0.5 FPS) at operating pressure and temperature. Flow of the gas stream containing inert gas, oxygen and water is preferably continued for an additional 2 hours after water partial pressure in the reactor outlet stream exceeds about 5.24 kPaa (0.76 psia) and preferably for up to about 90 minutes longer to insure that the catalyst is saturated with water at the water partial pressure employed and that metals are completely oxidized.

Oxyhalogenation (Step (b) of Invention)

The catalytic metals at this point in the regeneration procedure are typically agglomerated. Metal halide (chloride) molecules are mobile and disperse across the zeolite surfaces with facility. In step (b), the metals are halogenated (chlorinated) by exposure to oxygen, water and a source of halogen (chlorine) all in an inert carrier gas. Preferably the source of halogen in step (b) is a source of chlorine, such as Cl_2 , HCl , chlorinated hydrocarbons, such as carbon tetrachloride and mixtures of two or more thereof, most preferably HCl .

Oxyhalogenation is for example carried out at a pressure of about atmospheric to 2.07 MPaa (300 psia), preferably to 1.38 MPaa (200 psia), more preferably from 345 kPaa (50 psia) to 1.38 MPaa (200 psia), and most preferably at about 1.28 MPaa (185 psia). Oxychlorination temperatures are for example from 480°C to 550°C, preferably 500°C to 530°C, and most preferably

This Sheet Has Been Replaced

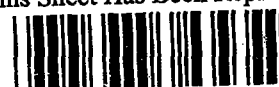


at about 510°C. Inert gas flow rate is preferably adjusted to make the linear gas velocity in the reactors above 15.2 cm/sec (0.5 FPS) at operating pressure and temperature. HCl is a preferred chlorine source because HCl converts to chlorine by reaction with oxygen via the Deacon reaction so chlorine is really the active chlorinating agent. Water partial pressure in the reactor inlet gas is for example up to 20.7 kPaa (3.0 psia), preferably to 13.8 kPaa (2 psia), and most preferably from 1.38 kPaa (0.2 psia) to 13.8 kPaa (2 psia). Oxygen partial pressure is for example up to 69 kPaa (10 psia), preferably from 6.9 kPaa (1 psia) to 34.5 kPaa (5 psia), and more preferably from 6.9 kPaa (1 psia) to 13.8 kPaa (2 psia). Halogen source (HCl) partial pressure in the reactor inlet gas is for example up to 3.45 kPaa (0.5 psia), preferably from 138 Paa (0.02 psia) to 3.45 kPaa (0.5 psia), and more preferably from 138 Paa (0.02 psia) to 2.07 kPaa (0.3 psia), and most preferably from 138 Paa (0.02 psia) to 1.38 kPaa (0.2 psia).

Completion of oxychlorination step (b) is signaled by appearance of chlorine and HCl, referred to herein as chlorine breakthrough, in the reactor effluent gas at a partial pressure preferably greater than 69 Paa (0.01 psia). Time to chlorine breakthrough after initiation of HCl flow is proportional to the chlorine feed rate and is inversely proportional to the amount of catalyst in the reactors; it typically takes from 2 to 6 hours.

After chlorine breakthrough, oxychlorination is preferably continued for an additional time period of up to 6 hours, preferably for from 2 hours to 5 hours.

In a manner similar to coke burn step (a), the gas stream from (b) may be recycled, i.e., recirculated, from the tail reactor to the lead reactor, where a



- 20 -

THIS SHEET HAS BEEN
REPLACED

series of two or more reactors is used, in order to conserve nitrogen of the inert carrier gas by employing an in-line recycle gas compressor. Preferably, about 10% of the recycle gas flow is purged with the purged amount being replaced with fresh oxychlorination gas prior to recirculating the stream.

Post Oxychlorination Cool Down(Optional Step (b'))

Higher regenerated catalyst activity is obtained when the post oxychlorination steps are conducted at lower temperature, i.e., within the range of 300°C to 400°C, and preferably at about 345°C, than the oxychlorination temperature which is from 450°C to 550°C. Preferably, the catalyst is cooled from oxychlorination temperature to a lower post treat temperature prior to oxychlorination post treatment. Thus, in this embodiment, between steps (b) and (c) there is performed a cooling step (b') comprising contacting the oxyhalogenated catalyst of step (b) with a gaseous stream comprising inert gas and/or oxygen and/or water and/or a source of halogen, preferably the gaseous stream of step (b), which gaseous stream is at a temperature effective to reduce the temperature of the catalyst to a value of from 300 to 400 °C. Preferably the cooling is done under an oxychlorination atmosphere to prevent premature reduction and agglomeration of catalytic metals. In this embodiment of the present invention, cool down is accomplished by continuing the flow of oxychlorination feed gas, for example having a HCl partial pressure of up to 3.45 kPaa (0.5 psia), preferably from 138 Paa (0.02 psia) to 3.45 kPaa (0.5 psia), more preferably 138 Paa (0.02 psia) to 2.07 kPaa (0.3 psia), and most preferably 138 Paa (0.02 psia) and 1.38 kPaa (0.2 psia). Alternatively, a gas which is essentially devoid of HCl can be used in this stage while reducing the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

- 21 -

temperature. The time required to cool the catalyst down to such lower temperatures, however, depends on the characteristics of the equipment in the plant and the temperature drop specified. Cool down does not
5 impair regenerated catalyst performance when done under an oxychlorination atmosphere.

Post-Oxychlorination Stripping (Step (c) of Invention)

It has been discovered that it is beneficial to regenerated catalyst activity to remove halogen
10 (chlorine) from the catalyst prior to the final reduction, and that the more chlorine removed before the final hydrogen reduction, the higher the activity of the regenerated catalyst. Essential and preferred conditions for step (c), and the reasons therefore, are
15 discussed hereinbefore. Step (c) is preferably accomplished by exposing the catalyst to a stream of inert gas containing oxygen at the lowest pressure, i.e., atmospheric pressure or even vacuum, which can be used depending on the circumstances. However, pressures
20 as high as 448 kPaa (65 psia), and preferably at about atmospheric may be used in certain situations. Temperature during this stripping step is from 300°C to 400°C, with 345°C being preferred. Water may be present in the treat gas during stripping step (c), for
25 example at a partial pressure of up to 20.7 kPaa (3 psia), preferably up to 13.8 kPaa (2 psia), more preferably 6.9 kPaa (1 psia), and most preferably 1.38 kPaa (0.2 psia) to 4.14 kPaa (0.6 psia). Where water is included in the gas flow, the
30 stripping is referred to herein as a wet stripping. Oxygen partial pressure in step (c) is for example up to 31 kPaa (4.5 psia), preferably up to 20.7 kPaa (3 psia), and more preferably 4.83 kPaa (0.7 psia) to 20.7 kPaa (3 psia). The inert gas flow rate during this
35 stripping step is preferably fixed to maintain at least

This Sheet Has Been Replaced



15.2 cm/sec (0.5 FPS) linear gas velocity through the catalyst beds.

Wet stripping in the previously described manner is continued until HCl partial pressure in the reactor effluent, i.e., exhaust HCl partial pressure, falls below 27.6 Paa (0.004 psia), preferably below 10.3 Paa (0.0015 psia) and more preferably below 4.8 Paa (0.0007 psia); exhaust HCl partial pressure in this range signals that chlorine concentration on the catalyst is acceptably low. Typically, exhaust HCl partial pressure falls into the 27.6 Paa (0.004 psia) to 4.8 Paa (0.0007 psia) range after 2 to 12 hours of wet stripping treatment.

Optionally, water flow may be then discontinued and the flow of inert gas and oxygen continued for about one hour to dry the system to prepare for the subsequent hydrogen reduction. The water partial pressure at the reactor outlet is then preferably less than 27.6 Paa (0.004 psia), more preferably less than 20.6 Paa (0.003 psia), and most preferably less than 10.3 Paa (0.0015 psia). In this embodiment, oxygen flow is cut off and inert gas flow is continued for about one hour to purge oxygen out of the reactor system prior to introducing hydrogen.

Alternatively, the stripping or soaking can be performed with a substantially dry gas stream having a partial pressure of water of essentially zero.

As in the hydrogen reduction step, these stripping steps, which are most preferably performed at atmospheric pressure, use once-through gas, which is then exhausted or purged from the outlet of the reactor vessel. In a reactor train, the gas would be purged or exhausted from the downstream tail reactor. Alternatively, this step can be performed using recycle gas at a pressure up to 448 kPaa (65 psia).



THIS SHEET HAS BEEN
REPLACED

- 23 -

Final Hydrogen Reduction (Step (d) of Invention)

The final step in the regeneration procedure is to reduce the catalytic metals, which at this point are dispersed in the zeolite as chloride molecules, to their zero valent metallic state without substantial agglomeration. Preferably a gaseous stream comprising inert gas which is substantially devoid of oxygen is passed for a time sufficient to lower oxygen partial pressure to below 138 Paa (0.02 psia) so as to avoid formation of an explosive mixture when hydrogen is added. Then reduction in accordance with the present invention is accomplished by introducing hydrogen, for example, at a partial pressure greater than 103 Paa (0.015 psia), preferably 103 Paa (0.015 psia) to 101 kPaa (14.7 psia), more preferably 1.03 kPaa (0.15 psia) to 34.5 kPaa (5 psia), and most preferably 6.9 kPaa (1 psia) to 20.7 kPaa (3 psia), into the inert gas flowing to the reactors, which induces rapid evolution of hydrogen halide into the treat gas. However, towards the end of this step a gas flow which is essentially 100% hydrogen could be used, making the inert gas optional. Thus, hydrogen halide, e.g., HCl partial pressure rises as the reduction treat gas, in this step the inert gas including hydrogen, moves downstream through the catalyst. Initially (first few minutes of reduction) a high level of hydrogen halide is released and moves rapidly through the catalyst bed. After this wave of hydrogen halide, it is desirable to minimize hydrogen halide partial pressure, preferably to less than 138 Paa (0.02 psia). This step is continued until an endpoint HCl partial pressure at the reactor outlet is less than 51.7 Paa (0.0075 psia). It has been discovered that reactions between HCl and unreduced catalyst downstream of the reaction front impair regenerated catalyst activity. Accordingly, the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

reduction is conducted to minimize the interaction between HCl and unreduced catalyst. In order to minimize these undesirable reactions, reduction is preferably performed at low temperature relative to oxychlorination step (b) temperature, for example, at a temperature of 300°C to 400°C, and preferably at about 345°C. Also, reduction is performed at low pressure, preferably at the lowest practicable pressure, i.e., about atmospheric pressure, and hydrogen addition rate is controlled to minimize hydrogen halide partial pressure throughout the reduction. Gas velocity through the catalyst bed is preferably maintained at above 15.2 cm/sec (0.5 FPS) for good gas contacting. Reduction time of one to seven hours has been discovered to be suitable for insuring complete reduction, with up to six hours being preferred.

As in the previous reduction step, this stage of hydrogen reduction, which is most preferably performed at atmospheric pressure, uses once-through hydrogen with nitrogen as the inert carrier gas, which is then purged downstream of the tail reactor. Alternatively, this step can be performed using recycled hydrogen and nitrogen for example at a pressure up to 448 kPaa (65 psia).

An alternative of the steps after wet post-oxychlorination stripping is to purge the catalyst with wet nitrogen and follow by wet hydrogen reduction. In this case, water is present, for example at a partial pressure at the reactor inlet up to 20.7 kPaa (3 psia), preferably to 13.8 kPaa (2 psia), more preferably 6.9 kPaa (1 psia) to 0.01 psia, and most preferably 1.38 kPaa (0.2 psia) to 4.14 kPaa (0.6 psia). However, the catalyst has to be dried out after wet reduction, before introducing hydrocarbon feed into the reactor, for example to a water partial pressure

This Sheet Has Been Replaced



- 25 -

THIS SHEET HAS BEEN
REPLACED

less than 27.6 Paa (0.004 psia), preferably less than
20.7 Paa (0.003 psia), and more preferably less than
10.3 Paa (0.0015 psia).

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

EXAMPLES

The following examples illustrate the invention.

EXAMPLE I

The catalyst used was an extrudate of zeolite L
5 bound with alumina containing 0.64 wt. % platinum. The
catalyst was run at reforming conditions. It contained
1 wt. % coke when the reforming run was terminated.
The catalyst was regenerated at 1.27 MPaa (185 psia)
using the following procedural stages. Linear gas
10 velocity through the catalyst was 15.2 cm/sec (0.5 fps)
and the inert carrier gas was nitrogen:

1. Coke burn step (a1) at 445°C for two hours
with 1 vol. % oxygen, (12.8 kPaa/1.85 psia partial
pressure).
- 15 2. Coke burn step (a2) at 510°C for 14 hours
with 3 vol% oxygen (38.3 kPaa/5.55 psia partial
pressure).
3. Oxychlorination step (b) at 510°C for three
hours with 600 vppm HCl, 0.66 vol. % water vapor, and
20 0.84 vol. % oxygen.
4. Cool down step (b) to 345°C over four hours
under oxychlorination atmosphere.
5. Stripping step for three hours with 0.66 vol.
% water vapor and 0.84 vol. % oxygen, to an HCl partial
25 pressure of 447 Paa (0.0648 psia).
6. Stripping step with 0.84 vol. % oxygen for
one hour.
7. Purge with nitrogen for one hour.
8. Reduction step with 0.2 vol. % hydrogen for
30 2.5 hours to an HCl partial pressure of which fell from
a value of 510 Paa (0.074 psia) immediately after the
initial HCl wave, to a final value of 76.5 Paa (0.0111
psia).

The catalyst regenerated with this procedure
35 (outside the scope of the invention) is designated as

This Sheet Has Been Replaced



- 27 -

THIS SHEET HAS BEEN
REPLACED

Catalyst A. A sample of the same catalyst was regenerated using the steps 1 through 4; followed by steps 5 through 8 which were modified as follows:

5 5a. Stripping step (c) at 345°C with 10 vol. % oxygen and 3 vol. % water in nitrogen at atmospheric pressure for three hours to an HCl partial pressure of 3.0 Paa (0.00044 psia).

10 6a. Stripping step (c) at 345°C with 10 vol. % oxygen in nitrogen for one hour at atmospheric pressure.

7a. Purge with nitrogen for one hour at atmospheric pressure.

15 8a. Reduce with hydrogen 10 vol. % for 2.5 hours at atmospheric pressure to an HCl partial pressure of which fell from a value of 75.8 Paa (0.011 psia) immediately after the HCl initial wave, to a final value of 6.0 Paa (0.00088 psia).

The catalyst regenerated with this modified procedure according to the invention is designated as
20 Catalyst B. The activity of Catalyst A and B was compared by running both at reforming conditions for 46 hours and then determining their benzene yield and selectivities. The test conditions were: 510°C; 8 weight hourly space velocity (whsv); 738 kPaa (107
25 psia); 4.25 hydrogen to oil molar ratio; on a feed comprising 40 wt. % normal hexane and 60 wt. % 3 methylpentane.

	CATALYST	Bz YIELD. WT. %	Bz SELECTIVITY
	WT. %		
30	A	26	64
	B	34	69

This example shows that if the post
oxychlorination stripping step is done at low
(atmospheric) pressure rather than at the higher
35 (conventional) oxychlorination pressure (1.27 MPaa),

This Sheet Has Been Replaced



- 28 -

THIS SHEET HAS BEEN
REPLACED

thus enabling a hydrogen halide partial pressure in the step (c) effluent gas of less than 27.6 Paa (0.004 psia), especially less than 10.3 Paa (0.0015 psia), the activity and selectivity of the regenerated catalyst is significantly higher.

Example II

The catalyst of Example I was subjected to a regeneration procedure entirely performed at atmospheric pressure. The linear velocity of gas flowing through the reactor was 15.2 cm/sec (0.5 fps) and the inert carrier gas was nitrogen.

The catalyst was dried under flowing nitrogen at 250°C for 12 hours. The catalyst was coke burned (step (a1)) at 445°C with 2.6 vol. % oxygen in nitrogen for two hours and then (step (a2)) at 510°C with 20 vol. % oxygen for 22 hours. Oxygen was purged from the reactor by cutting off oxygen flow and continuing nitrogen flow for 30 minutes.

The catalyst was reduced (step (a')) by passing hydrogen over it at 510°C for one hour. Hydrogen was purged from the reactor by passing nitrogen through the reactor for thirty minutes.

Platinum in the catalyst was redispersed (step (b)) with a gas containing 0.3 vol. % HCl, 3.4 vol. % water vapor, and 10 vol. % oxygen at 510°C for six hours. Temperature was reduced (step (b')) to 345°C. The catalyst was stripped to less than the minimum detectable level of 3.0 Paa (0.00044 psia), of residual HCl (step (c)) with air containing 3.4 vol. % water vapor at 345°C for one hour. Air was purged from the reactor with nitrogen and the catalyst was reduced (step (d)) with a gas stream containing 20 vol. % hydrogen in nitrogen at 345°C for one hour to an HCl partial pressure of less than 3.0 Paa (0.00044 psia). This regenerated catalyst is designated Catalyst C.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

The experiment was repeated with another three gram sample of the coked catalyst except that the catalyst was not reduced with hydrogen (step (a')) after the coke burn (step (a1) and (a2)). The catalyst regenerated without preoxychlorination hydrogen reduction is designated Catalyst D.

Catalyst C and D, each regenerated according to the invention, were tested for reforming activity and benzene selectivity by the method described in Example I.

CATALYST	Bz YIELD. WT. %	Bz SELECTIVITY
WT. %		
C	33.7	68
D	25.5	64

The activity and selectivity of catalyst C which was reduced with hydrogen after coke burn and before oxychlorination was significantly higher than that of catalyst D.

Example III

This example shows that preoxychlorination reduction with hydrogen (step (a')) after coke burn (step (a)), and post oxychlorination stripping (step (c)) at low (atmospheric) pressure rather than at oxychlorination (step (b)) pressure 1.20 MPaa (175 psia) improves recovery of activity and selectivity. The deactivated catalyst of Example I was regenerated using the following procedure:

The catalyst was coke burned (a1) at 450°C and 1.20 MPaa (175 psia) for 10 hours with 0.2 vol. % oxygen in nitrogen. Linear gas velocity was maintained at 15.2 cm/sec for the entire regeneration procedure. The coke burn was completed (a2) at 510°C and 175 psia. The catalyst was oxychlorinated (b) to redisperse platinum by adding 0.15 vol. % HCl to the gas stream flowing into the reactor for 4.5 hours. Then, the

This Sheet Has Been Replaced



REPLACED

- 30 -

catalyst was cooled (b') from 510°C to 345°C while continuing the flow of the HCl/oxygen/nitrogen oxychlorination gas mixture. The catalyst was then stripped (c) at 1.17 MPaa (170 psia) and 345° C by
5 passing a gas stream containing 0.87 vol. % oxygen and 0.84 vol. % water vapor in nitrogen through the catalyst. Stripping was completed by cutting off water vapor flow and continuing flow of the oxygen in nitrogen stream at 1.17 MPaa (170 psia) and 345°C for
10 one more hour. Oxygen flow was cut off and nitrogen flow was continued to purge oxygen out of the reactor system. Then the catalyst was reduced by passing 2 vol. % hydrogen in nitrogen at 345°C and 1.17 MPaa (170 psia) through the catalyst for two hours. This
15 regenerated catalyst is designated E (not in accordance with the invention).

The same deactivated catalyst was regenerated using the preferred procedure of the invention. The catalyst was coke burned (a1) at 450°C and 1.17 MPaa
20 (170 psia) with 0.2 vol. % oxygen in nitrogen for 10 hours and then (a2) at 510°C with 3.5 vol. % oxygen for 16 hours. Linear gas velocity through the catalyst was 15.2 cm/sec throughout the regeneration procedure and the inert carrier gas was nitrogen. Oxygen was purged
25 out of the reactor system by continuing nitrogen flow after cutting off oxygen and then the catalyst was reduced (a') with 50% hydrogen in nitrogen at 510°C for one hour. Hydrogen was purged out of the reactor system by continuing nitrogen flow after cutting off
30 hydrogen and then the catalyst was preconditioned (a'') for oxychlorination by treating it with 0.89 vol. % oxygen and 0.87 vol. % water vapor at 510°C and 1.20 MPaa (175 psia). The catalyst was oxychlorinated (b) to redisperse platinum by adding 0.15 vol. % HCl to the
35 carrier gas stream. The catalyst was stripped (c) at

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

- 31 -

345°C at atmospheric pressure with a gas stream containing 5 vol. % oxygen and 0.84 vol. % water vapor for eight hours to an HCl partial pressure of 10.3 Paa (0.0015 psia). Water vapor flow was cut off and the catalyst treated with dry oxygen in nitrogen mixture for two hours. Oxygen was purged out of the system by continuing nitrogen flow for two hours. Finally, the catalyst was reduced (d) at 345°C with 7 vol. % hydrogen in nitrogen for six hours to an HCl partial pressure of 7.6 Paa (0.0011 psia). This regenerated catalyst, designated F, is regenerated according to the invention.

Catalyst F exhibited 30% higher activity and selectivity for aromatizing hexane streams to benzene than did Catalyst E, when subjected to the test described in Example I.

As evidenced by the Examples, the process of the invention is one which preferably will regenerate a catalyst after use in reforming processes, to a benzene activity which is at least 25 percent greater than the activity of an equivalently coked catalyst that has been regenerated by a conventional procedure not including the parameters specified for steps (c) and (d). The process of the invention is also effective to increase the activity of fresh catalyst which has not yet been subjected to reforming reactions, preferably to a benzene activity amounting to a weight percent benzene yield which is at least 1.5 wt% greater than the untreated, low activity catalyst. In each case, the activity test employed is as described in Example I.

This Sheet Has Been Replaced



- 32 -

THIS SHEET HAS BEEN
REPLACEDCLAIMS:

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

5 (a) contacting the deactivated or low activity catalyst with a gaseous stream comprising inert gas and oxygen under oxidation conditions for a time effective to burn coke off the deactivated or low activity catalyst to result in a substantially decoked catalyst;

10 (b) contacting the substantially decoked catalyst with a gaseous stream comprising inert gas, oxygen, water and a source of halogen under oxyhalogenation conditions comprising a temperature of from 450°C to 550°C and a time effective to halogenate and disperse
15 the metal to result in a halogenated catalyst comprising dispersed halogen-complexed metal;

(c) contacting the halogenated catalyst with a gaseous stream comprising inert gas and oxygen under halogen removal conditions comprising a temperature of
20 from 300°C to 400°C, a low total pressure and a time effective to remove from the halogenated catalyst at least some of the halogen complexed to the metal and result in a gaseous stream after contact with the catalyst comprising hydrogen halide at a partial
25 pressure of less than 27.6 Paa (0.004 psia); and

(d) contacting the halogenated catalyst from step (c) with a gaseous stream comprising hydrogen under reducing conditions comprising a low total pressure for a time effective to reduce at least some of the
30 halogen-complexed metal in the catalyst to the metallic state and result in a regenerated catalyst comprising dispersed metal and zeolite and a gas flow after contact with the catalyst comprising hydrogen halide at a partial pressure of less than 51.7 Paa (0.0075 psia).

35

This Sheet Has Been Replaced


THIS SHEET HAS BEEN
REPLACED

- 33 -

2. A process according to claim 1 wherein step (a) is performed at a temperature of from 400 to 550°C and/or a pressure of from sub-atmospheric to 2.07 MPaa (300 psia) and/or an oxygen partial pressure not more than
5 69 kPaa (10 psia).

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
10 partial pressure of carbon dioxide of less than 69 Paa (0.01 psia).

4. A process according to any preceding claim wherein the gaseous stream in step (a) additionally comprises
15 water and/or a source of halogen.

5. A process according to any preceding claim wherein step (a) is performed in a first stage (a1) and a second stage (a2), wherein (i) stage (a1) is performed
20 at a lower temperature than stage (a2) and/or (ii) the gaseous stream of stage (a1) has a lower oxygen concentration than that of stage (a2).

6. A process according to any preceding claim wherein
25 step (b) is performed at an oxygen partial pressure not greater than 69 kPaa (10 psia) and/or a water partial pressure not greater than 20.7 kPaa (3 psia) and/or a halogen source partial pressure prior to contact with the catalyst of not less than 138 Paa (0.02 psia)
30 and/or a total pressure of not more than 2.07 MPaa (300 psia).

7. A process according to any preceding claim wherein in step (b) the gaseous stream after contact with the



This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

substantially decoked catalyst comprises a partial pressure of halogen of at least 69 Paa (0.01 psia).

5 8. A process according to any preceding claim wherein step (c) is performed at a total pressure not greater than 690 kPaa (100 psia), preferably from sub-atmospheric to 448 kPaa (65 psia).

10 9. 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 halogenated catalyst comprises a partial pressure of hydrogen halide of less than 10.3 Paa (0.0015 psia), preferably less than 4.8 Paa (0.0007 psia).

15 10. A process according to any preceding claim wherein the gaseous stream in step (c) additionally comprises water and/or is performed at an oxygen partial pressure not greater than 31 kPaa (4.5 psia).

20 11. A process according to any preceding claim wherein step (d) is performed at a temperature of from 300 to 400°C and/or a hydrogen partial pressure greater than 103 Paa (0.015 psia) and/or with the additional
25 presence of water in the gaseous stream.

12. A process according to any preceding claim wherein step (d) is performed at a total pressure not greater than 448 kPaa (65 psia); preferably from sub-
30 atmospheric to 448 kPaa (65 psia).

13. A process according to any preceding claim wherein in step (a) and/or step (b) at least a portion of the gaseous stream after contact with the catalyst is
35 recycled to the respective step, and/or in step (c)



This Sheet Has Been Replaced

A standard 1D barcode with vertical black bars of varying widths on a white background, tilted slightly to the right.

THIS SHEET HAS BEEN REPLACED

and/or (d) none of the gaseous stream after contact with the catalyst is recycled to the respective step.

14. A process according to any preceding claim wherein
5 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
conditions for a time effective to reduce the metal
10 component of the catalyst to the metallic state.

15. A process according to claim 14 wherein step (a')
is performed at a hydrogen partial pressure greater
than 103 Paa (0.015 psia) and/or a temperature of from
15 300 to 550°C and/or a total pressure not greater than
2.07 MPaa (300 psia) and/or with the additional
presence of water in the gaseous stream.

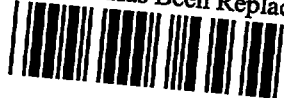
16. A process according to any preceding claim wherein
20 between steps (a) and (b) there is performed a catalyst
conditioning step (a'') comprising contacting the
catalyst with a gaseous stream comprising inert gas,
oxygen and water under conditions and for a time to
saturate the catalyst with water and form a
25 substantially water saturated catalyst.

17. A process according to claim 16 wherein the
substantially saturated catalyst has a moisture content
in equilibrium with the gaseous stream of step (a'').
30

18. A process according to claim 16 or 17 wherein step
(a'') is performed at a temperature of from 300 to 550°
C and/or a water partial pressure not greater than 20.7
kPaa (3 psia) and/or an oxygen partial pressure not



This Sheet Has Been Replaced

A standard 1D barcode with vertical bars of varying widths.

- 36 -

**THIS SHEET HAS BEEN
REPLACED**

greater than 69 kPaa (10 psia) and/or a total pressure not greater than 2.07 MPaa (300 psia).

19. A process according to any preceding claim wherein
5 between steps (b) and (c) there is performed a cooling step (b') comprising contacting the oxyhalogenated catalyst of step (b) with a gaseous stream comprising inert gas and/or oxygen and/or water and/or a source of halogen, preferably the gaseous stream of step (b),
10 which gaseous stream is at a temperature effective to reduce the temperature of the catalyst to a value of from 300 to 400°C.

20. A process according to any preceding claim wherein
15 the reforming 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 present as from 0.05 to 6 wt% of the catalyst, which
20 optionally comprises a binder.

21. A process according to any preceding claim wherein the regenerated catalyst produced in step (d): (i) is produced from a deactivated (coked) catalyst and has an
25 activity for aromatizing hexanes to benzene in accordance with the test defined in Example I hereof which is at least 25 percent greater than that of a catalyst which has been regenerated by a procedure not including the operating parameters of steps (c) and (d)
30 as defined in claim 1; or (ii) is produced from a low activity catalyst and has an activity for aromatizing hexanes to benzene in accordance with the test defined in Example I hereof, measured in weight percent yield of benzene, which is at least 1.5 wt% greater than the



This Sheet Has Been Replaced



- 37 -

THIS SHEET HAS BEEN
REPLACED

activity of the low activity catalyst before
regeneration according to the invention.

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



This Sheet Has Been Replaced

