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LOW TEMPERATURE REGENERATION OF
COKE DEACTIVATED REFORMING CATALYSTS

BACKGROUND OF THE INVENTION

The subject of the present invention is a process for the regeneration of a hydrocarbon reforming catalyst which has been deactivated due to buildup of carbonaceous material on the catalyst. More specifically, the present invention provides a method for regenerating a coke deactivated reforming catalyst by a controlled low temperature carbon-burn procedure which results in the catalyst having activity, selectivity and stability characteristics approximating, or which are even better than, the catalyst prior to the buildup of carbon. The reforming catalysts intended to be regenerated by the process of the present invention comprise a molecular sieve material and platinum.

Platinum containing catalysts are widely used in the oil refining and petrochemical industries, and are particularly important in a reforming process where paraffins, olefins and naphthenes are converted to aromatic compounds. Conventional reforming catalysts typically include one or more metals, most typically platinum, dispersed on a base, and may also include a binding agent for adding physical support to the base, and chloride to provide an acidic function. Typically, the catalyst base is alumina, but recently molecular sieve based catalysts have been found to be effective for reforming reactions.

Catalytic compositions containing zeolites are well known in the industry and recently the use of L-zeolites in combination with other specified catalytic components have been found to be particularly preferred for reforming. The

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01 aromatic compounds produced by such a catalytic conversion
02 are valuable to a refiner due to their higher octane rating,
03 and may be recovered from the reforming product for further
04 processing and reaction in the petrochemical industries.
05 The L-zeolite catalysts are particularly effective for
06 converting C₆ and C₇ non-aromatic hydrocarbons which normally
07 boil between 125°F and 225°F, to benzene and toluene.

08

09 In the reforming process, a hydrocarbon feedstock is passed
10 through a catalyst-containing reactor in the presence of
11 hydrogen at an elevated temperature. In the reactor and
12 upon contact with the reduced or activated catalyst, some of
13 the paraffins, olefins and naphthenes in the feedstock react
14 to form a more desired, higher octane aromatic product. In
15 the course of typical reforming operations, the catalysts
16 will typically become deactivated due to the deposition of
17 carbonaceous material or "coke" upon the catalyst, and/or
18 sintering or poisoning of the catalytic metal particles. In
19 commercial practice, the deactivated catalyst will then be
20 regenerated by a process which may include as a step the
21 exposing of the catalyst to an oxygen containing gas at
22 elevated temperature (typically 950°F final burn
23 temperature) to burn the carbonaceous deposits accumulated
24 on the catalyst. However, prior to our present invention,
25 burning the coke off the catalyst at elevated temperatures
26 caused the catalytic metal to agglomerate, which
27 significantly lowered the activity and thus worsened the
28 performance of the catalyst. Consequently, specific steps
29 directed to the redispersion of the catalytic metal on the
30 base were necessary. The redispersion steps typically
31 comprise contacting the catalyst with a chloride containing
32 gas in the presence of oxygen and water vapor, and are well
33 known in the art.

34

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01 In U.S. Patent No. 4,493,901 issued January 15, 1985 to
02 Bernard et al., a method of regenerating a catalyst
03 comprising platinum and a non-acidic L-zeolite is described,
04 whereby the catalyst is subjected to a multi-step process,
05 the first step being exposure to a hydrogen environment,
06 followed by a carbon burn step, and then a calcination step
07 followed specifically by an oxychlorination step. The
08 regeneration method of Bernard et al. utilizes a hydration
09 step following the oxychlorination step. In the hydration
10 step, a quantity of water is added to the cooling air.

11
12 In U.S. Patent No. 4,810,683, issued March 7, 1989, to Cohn,
13 a method is described which utilizes a halogen or halogen
14 containing gas during the carbon burn step. The burning
15 step of the process of U.S. Patent No. 4,810,683 occurred
16 necessarily in the presence of a halogen or halogen
17 containing gas and at a temperature of from 300°C to 600°C.

18
19 U.S. Patent No. 3,986,982, issued October 19, 1976, to
20 Crowson et al., describes a method for regenerating a
21 deactivated platinum group metal-loaded zeolites by burning
22 off deposits on the catalyst with a stream of inert gas and
23 oxygen at a temperature controlled to a maximum of 550°C.
24 Example 1 shows a stepwise burn procedure to 530°C. The
25 water content was held at 100-130 ppm. This was followed by
26 treating with a stream of an inert gas containing from 0.5
27 to 20.0 vol% oxygen and from 5 to 500 ppmv chlorine as
28 chlorine gas. The resultant catalyst is purged to remove
29 residual oxygen and chlorine and then reduced with hydrogen.

30
31 U.S. Patent No. 4,359,400, issued November 16, 1982, to
32 G. R. Landolt et al., describes a process whereby
33 multimetallic platinum containing catalysts are contacted
34 with oxygen containing gas at elevated temperatures to burn

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01 off coke and then treated with dry, oxygen-free hydrogen
02 halide. The catalyst is then treated with Cl₂ containing
03 gas which is oxygen and water-free.
04

05 U.S. Patent Number 4,719,189, issued January 12, 1988 to
06 A. S. Krishnamurthy describes a process for rejuvenating a
07 coke-deactivated nobel metal containing zeolite catalyst.
08 The process comprises contacting the catalyst with a mixture
09 of oxygen and sulfur dioxide, followed by catalyst
10 reduction. Temperatures from 752-840°F are preferred.
11

12 U.S. Patent No. 4,645,751, issued February 24, 1987, to
13 S. B. McCullen et al., describes a process for rejuvenating
14 a highly silicious (silica-alumina ratio of at least 20)
15 Pt zeolite catalyst wherein the Pt has become agglomerated.
16 The agglomerated catalyst is first reduced with hydrogen.
17 Following reduction the catalyst is treated with hydrogen
18 chloride and oxygen in an inert gas carrier at 400-450°C.
19

20 U.S. Patent No. 4,752,595, issued June 21, 1988, to
21 S. B. McCullen et al., describes a process for regenerating
22 a nobel-metal containing zeolite catalyst. The process
23 consists of a coke burn step followed by a low temperature
24 reduction step (212-482°F) Oxidizing conditions for the coke
25 burn include temperatures ranging from 392-1004°F,
26 preferably 752-950°F.
27

28 U.S. Patent No. 4,657,874, issued April 14, 1987, to
29 W. S. Borghard et al., describes a method where Pt on a
30 highly silicious zeolite is redispersed. The process
31 comprises a coke burn followed by oxychlorination. The
32 oxygen burn step is done under conditions that are
33 sufficiently mild to prevent any alteration in the crystal
34 structure of the zeolite. Example 6 uses a temperature of

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01 850°F. This is then followed by treating with a stream of
02 inert gas containing 6 to 15 Torr of chlorine gas and water
03 vapor such the molar ratio of water to chlorine gas is
04 between 0.01 and 2.0. Oxygen may also be present. The
05 rejuvenation is typically carried out at 450°C (842°F).
06

07 U.S. Patent No. 4,851,380, issued July 25, 1989, to
08 D. A. Van Leirsburg et al., describes a process for
09 regenerating a sulfur contaminated reforming catalyst. The
10 process includes a platinum agglomeration step which can be
11 accomplished by contacting the catalyst with O₂ between
12 800°F and 1200°F and an oxychlorination step. Pt
13 redispersion by contacting an agglomerated catalyst with
14 carbon monoxide and a sulfur free halogen acid gas.
15

16 U.S. Patent No. 4,855,269, issued August 8, 1989, to
17 D. H. Mohr, discloses a platinum redispersion method
18 comprising a wet oxychlorination step, followed by a
19 nitrogen purge, followed by reduction.
20

21 U.S. Patent No. 4,914,068 issued April 3, 1990, to
22 V. R. Cross, describes a process for the improved retention
23 of the platinum dispersion following oxychlorination if the
24 catalyst is cooled to 430°C or preferably less than 375°C
25 prior to start of reduction. Coke was burned off the
26 catalyst at 510°C prior to reduction.
27

28 Unfortunately, the presence of halogens such as chlorine or
29 fluorine or their compounds during regeneration results in
30 the formation of corrosive by-products such as HCl and
31 NH₄Cl. These compounds can cause damage to equipment used
32 in the reforming process such as heat exchangers, liquid/gas
33 separators and reactor internals. The halogen containing
34 compounds and their products necessary for platinum

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01 redispersion are highly toxic as well. Therefore, it is
02 highly desirable to have available a catalyst regeneration
03 procedure that does not include the use of a halogen
04 containing gas.

05
06 U.S. Patent No. 5,073,529, issued December 17, 1991 to
07 Miller et al., describes a process for regenerating a
08 coke-deactivated reforming catalyst. A two-step carbon burn
09 procedure is used wherein the catalyst is initially
10 contacted with oxygen and an inert gas at a temperature
11 ranging from 500-700°F. During the second step, the
12 catalyst is contacted with oxygen and an inert gas at a
13 temperature ranging from 850-950°F.

14
15 SUMMARY OF THE INVENTION
16

17 The present invention relates to a halogen-free process to
18 regenerate a coke contaminated catalyst comprising platinum
19 on a molecular sieve support which process comprises
20 contacting said catalyst with an oxygen-containing gas at a
21 temperature of from 300°F to no more than about 780°F. More
22 particularly, it relates to a process to regenerate a coke
23 contaminated catalyst comprising contacting said catalyst
24 with a halogen-free oxygen-containing gas at a maximum
25 temperature of less than 780°F for a sufficient period of
26 time such that the aromatization activity is restored to
27 within 20°F of the aromatization activity the catalyst
28 possessed at the start of the previous run cycle. By the
29 term "aromatization activity" we mean the extrapolated
30 start-of-run temperature where the run conditions and the
31 feed as well as the aromatics yield are substantially the
32 same as in the previous run cycle. By the practice of the
33 present invention, the platinum on the catalyst remains
34 sufficiently dispersed on the support to allow for an

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01 activity change of not more than 20°F upon termination of
02 the regeneration procedure, and return of the catalyst to
03 hydrocarbon conversion service. Thus, the catalyst
04 aromatization activity is based upon the temperature needed
05 to achieve a desired constant aromatics production.
06 Typically, we have controlled our process to about 40 to 42
07 wt.% aromatics in the product, although other values may be
08 set, in other circumstances. Regeneration by the process of
09 the present invention results in a catalyst which has an
10 aromatization activity, as defined above, which is within
11 20°F of the temperature needed in the previous run to
12 achieve the same constant aromatics production.

13
14 Among other factors, we have found that by limiting the
15 ultimate temperature in the carbon burn regeneration
16 procedure to a maximum temperature of less than 780°F,
17 preferably between 600°F to 750°F the catalyst may be
18 restored to an activity very close to that of the fresh
19 catalyst, without requiring a metal re-dispersion step. It
20 is further preferred the carbon burn be initiated at a
21 temperature of less than about 500°F and further that the
22 recycle gas be dried to achieve a water concentration in the
23 recycle gas of less than 1000 ppm water, prior to the
24 recycle gas entering the reforming reactor train.

25
26 We have found that by avoiding addition of a halogen or
27 halogen containing gas during or after the carbon burn
28 procedure, plant deterioration due to stress cracking and
29 corrosion is minimized. Further, prior to our present
30 invention, it was common practice to circulate soda ash or
31 morpholine solutions through effluent heat exchangers,
32 transfer lines, and liquid-gas separators during the
33 regeneration of reforming catalyst in order to prevent
34 corrosion due to chlorides. The need to use corrosion

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01 inhibitor solutions is eliminated when regenerating
02 reforming catalyst by the method of the present invention.

03

04 In general, the art teaches away, i.e., describes high
05 temperature burn procedure followed by redispersion step or,
06 burn/redispersion combined. We have now, surprisingly,
07 found that if the coke burn and reduction are both done at
08 low temperatures and with low concentration of water, the
09 regenerated catalyst has excellent activity and unexpectedly
10 long life.

11

12 Surprisingly, we have also found that the rate of
13 deactivation or "fouling rate" of the regenerated catalyst
14 decreases following the application of the regeneration
15 process of the present invention. Thus, a catalyst
16 regeneration procedure was discovered in which noble metal
17 does not appreciably agglomerate; eliminating the need for a
18 redispersion step, which are among the advantages of using
19 the present regeneration method on a Pt containing molecular
20 sieve type catalyst.

21

22 DETAILED DESCRIPTION OF THE INVENTION

23

24 As explained in the summary section above, the present
25 invention is a procedure for regenerating reforming
26 catalysts, comprising platinum on a molecular sieve support.

27

28 By the term "reforming" we mean the process of converting
29 paraffins, naphthenes or olefins to aromatic hydrocarbons
30 via hydrodecyclization or dehydrogenation. Feeds useful in
31 reforming typically include hydrocarbons having from six to
32 eleven carbon atoms, but these feeds can also include
33 narrower cuts, such as a C₆ to C₇ cut. Indeed, the reforming
34 catalysts that can be regenerated by the process of this

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01 invention can be used to make chemicals as well as gasoline
02 components. For example, benzene, toluene or mixtures
03 thereof can be produced by reforming hydrocarbons having six
04 to seven carbon atoms.

05

06 The catalysts advantageously regenerated by the method of
07 this invention comprise platinum on a molecular sieve
08 support. Molecular sieves are defined as porous materials
09 which exhibit the property of acting as sieves on a
10 molecular scale. The molecular sieves of most interest for
11 catalysis are those which have uniform pore sizes in the
12 4.2 to 15 Angstrom diameter range, particularly crystalline
13 materials of the aluminophosphate, aluminosilicate, and pure
14 silica types. The aluminosilicate molecular sieves include
15 zeolites and certain modified clays.

16

17 Examples of aluminophosphate molecular sieves include
18 ALPO-5, ALPO-11, ALPO-31, ALPO-34, and ALPO-41, as well as
19 isostructural materials containing silicon, cobalt,
20 manganese, magnesium, iron, chromium, titanium, or other
21 elements as part of the crystalline framework. Zeolite
22 molecular sieves of particular interest include zeolite
23 types X, Y, and L, mordenite, ZSM-5, ZSM-12, ZSM-20, SSZ-25,
24 SSZ-26, and beta zeolite. Examples of modified clays with
25 molecular sieving properties include pillared bentonites and
26 hectorites. Silicalite and SSZ-24 are examples of molecular
27 sieves composed of substantially silica. Silicalite has the
28 same crystal structure as ZSM-5 except that substantially
29 all of the aluminum atoms have been replaced with silicon
30 atoms. SSZ-24 is the all-silica structural analog of
31 ALPO-5.

32

33

34

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01 Catalyst Description

02

03 In copending Application Serial No. 496,119, assigned to the
04 assignee of the present invention and entirely incorporated
05 by reference herein, an intermediate pore size crystalline
06 silicate having a silica to alumina ratio of preferably at
07 least 500, is described. We have found the present catalyst
08 regeneration process may be advantageously used to
09 regenerate the intermediate pore size crystalline silicate
10 catalyst, and that the present process may also be
11 advantageously applied to a mixed catalyst system comprising
12 the intermediate pore size crystalline silicate described in
13 copending Application Serial No. 496,119.

14

15 A preferred catalyst to regenerate by the process of this
16 invention comprises platinum on an alkaline earth or alkali
17 metal exchanged, L-zeolite. It is especially preferred that
18 this catalyst be protected from sulfur poisoning during its
19 use in reforming, so that the catalyst is never contacted
20 with more than 100 ppb by weight sulfur in the feed. This
21 can be accomplished by using a sulfur converter/sorber
22 system as described in U.S. Patent No. 4,925,549 to Robinson
23 et al. The regeneration process of this invention is
24 especially effective on substantially sulfur free catalyst.

25

26 In addition to platinum, the catalysts regenerated by the
27 present invention may contain elements such as rhenium, tin,
28 germanium, iridium, copper, iron, cobalt, nickel, and
29 titanium which in certain cases may improve catalyst
30 selectivity or stability. For naphtha reforming, it is
31 desirable that the molecular sieve catalyst have a low
32 acidity. Acid sites may be neutralized by ion exchange with
33 alkali ions such as lithium, sodium, potassium, cesium and
34 rubidium ions or alkaline earth ions such as calcium,

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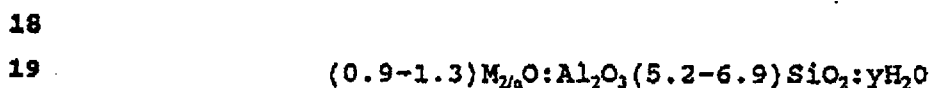


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01 magnesium, strontium, and barium. With zeolites, low
02 acidity may also be achieved by substituting boron for
03 aluminum in the zeolite framework; for example, boron
04 substituted beta zeolites or by using a zeolite with a
05 silica/alumina ratio greater than 500.

06
07 The present invention has been found to be particularly
08 effective when applied to large-pore zeolites. Large-pore
09 zeolites are defined as zeolites having an effective pore
10 diameter of between 6 and 15 Angstroms. Among the
11 large-pore zeolites which have been found to be useful as
12 reforming catalysts, L-type zeolites are the most important.
13 Other important zeolites include X-zeolites, Y-zeolites,
14 mordenites, and zeolite beta.

15
16 A typical composition of L-type zeolites, expressed in terms
17 of mole ratios of oxides, may be represented as follows:



21 wherein M designates a cation, n represents the valance of
22 M, and y may be any value from 0 to 9. Zeolite L, its X-ray
23 diffraction pattern, its properties and method for its
24 preparation are described in detail in U.S. Patent
25 No. 3,216,789 which is hereby incorporated by reference.
26 The true formula may vary without changing the crystalline
27 structure. For example, the mole ratio of silicon to
28 aluminum (Si/Al) may vary from over a range which is
29 typically 1.5 to 3.5, but may be higher. The barium
30 exchanged form of zeolite L is particularly preferred as
31 described, for example, in U.S. Patent Nos. 4,434,311 and
32 4,547,472.

33
34

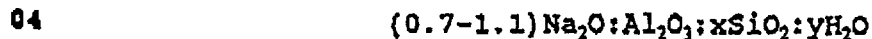
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01 The chemical formula for zeolite Y expressed in terms of
02 oxide molar ratio may be written as:

03



05

06 wherein x is a value between 3 and 6, and y may be a value
07 up to 9. Zeolite Y has a characteristic X-ray diffraction
08 pattern which may be employed with the above formula for
09 identification. Zeolite Y is described in more detail in
10 U.S. Patent No. 3,130,007. U.S. Patent No. 3,130,007 is
11 hereby incorporated by reference herein to show a zeolite
12 useful in the present invention.

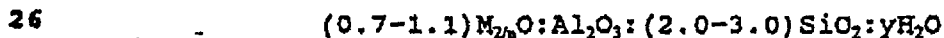
13

14 More recent patents disclose high silica/alumina versions of
15 zeolite Y produced by steaming and/or chemical extraction
16 which removes aluminum from the framework of the originally
17 synthesized zeolite. Y-zeolites with framework
18 silica/alumina ratios as high as 50:1 or higher may be
19 prepared by these methods, and are useful supports for the
20 reforming catalysts regenerated by the method of the present
21 invention.

22

23 Zeolite X is a synthetic crystalline zeolitic molecular
24 sieve which may be represented by the formula:

25



27

28 wherein M represents a metal, particularly alkali and
29 alkaline earth metals, n is the valence of M, and y may have
30 any value up to about 8 depending upon the identity of M and
31 the degree of hydration of the crystalline zeolite.

32 Zeolite X, its x-ray diffraction pattern, its properties and
33 method for its preparation are described in detail in U.S.
34 Patent No. 2,882,244, which is hereby incorporated by



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01 reference in its entirety to show a zeolite useful in the
02 present invention.

03

04 Zeolite beta is a known synthetic crystalline
05 aluminosilicate originally described in U.S. Patent
06 Nos. 3,308,069 and RE 28,341 to which reference is made for
07 further details of this zeolite, its preparation and
08 properties. These references describe the composition of
09 zeolite beta in its as-synthesized form as follows:

10

11
$$[XNa(1.0 \pm 0.1 - X)TEA]AlO_2 \cdot Y(SiO_2 \cdot W H_2O)$$

12

13 where X is less than 1, preferably less than 0.75, TEA
14 represents tetraethylammonium ion, Y is greater than 5 and
15 less than 100, and W is up to about 4, depending on the
16 condition of dehydration and on the metal cation present.
17 These references also teach that the sodium ion may be
18 replaced by another metal ion using ion exchange techniques.
19 Subsequent publications such as European Patent Applications
20 Nos. 95,304; 159,846; 159,847; and 164,939 have broadened
21 the definition of zeolite beta to include materials prepared
22 using templating agents other than tetraethylammonium
23 hydroxide and materials having a Si/Al ratio greater than
24 100. Also the zeolite described in European Patent
25 Application No. 55,046 ("Nu-2") and British Patent
26 Application No. 2,024,790 ("Borolite B") have structures and
27 X-ray diffraction patterns similar to that of zeolite beta
28 and are included within the scope of the term "zeolite beta"
29 as used herein.

30

31 Mordenite is a commercially available zeolite which occurs
32 in nature and has also been synthesized. Both "small port"
33 and "large port" mordenites have been synthesized. The
34 "large port" form is preferred for catalysis and is

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01 described in "Zeolite Molecular Sieves" by Donald W. Breck,
02 published by John Wiley and Sons. A typical oxide
03 composition is:

04

05 $\text{Na}_2\text{O} \bullet \text{Al}_2\text{O}_3 \bullet 9-10 \text{ SiO}_2 \bullet 6 \text{ H}_2\text{O}$

06

07 The silica/alumina ratio may be increased by extracting
08 alumina using various chemical and thermal methods similar
09 to those employed with zeolite Y.

10

11 The percentage of platinum in the catalyst is between 0.1%
12 and 10%, the lower limit corresponding to minimum practical
13 catalyst activity and the upper limit to roughly the maximum
14 possible platinum utilization. Preferably, the catalyst
15 contains between 0.2 and 5.0 percent platinum. Group VIII
16 metals are introduced into a large-pore zeolite during
17 synthesis, impregnation or ion exchange in an aqueous
18 solution of an appropriate metal salt. If it is desired to
19 introduce two Group VIII metals onto the large-pore zeolite,
20 the operation may be carried out simultaneously or
21 sequentially.

22

23 By way of example, platinum can be introduced by
24 impregnating the large-pore zeolite with an aqueous solution
25 of tetrammineplatinum (II) nitrate $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$,
26 tetrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, or
27 diammineplatinum $[\text{Pt}(\text{NH}_3)_2](\text{NO}_2)_2$. In an ionic exchange
28 process, platinum can be introduced by using cationic
29 platinum complexes such as tetrammineplatinum (II) nitrate.

30

31 A binder may be used in the preparation of the catalysts.
32 An inorganic oxide is used as a matrix to bind the
33 large-pore zeolite. This binder can be a natural or a
34 synthetically produced inorganic oxide or combination of

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01 inorganic oxides. Typical inorganic oxide binders which can
02 be used include clays, alumina, silica or mixtures thereof.
03 Preferable binders are alumina, silica, or mixtures thereof.
04 Acidic sites on the binder are preferably exchanged by
05 cations which do not impart strong acidity (such as sodium,
06 potassium, rubidium, cesium, calcium, strontium or barium).
07

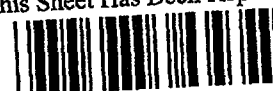
08 After the desired metal or metals have been introduced, the
09 catalyst is typically calcined in air and then reduced in a
10 hydrogen environment.
11

12 The regeneration process of the present invention may be
13 useful on catalysts in the physical form of extrusions,
14 spheres, pills, pellets, granules, broken fragments, or
15 various other shapes known in the art.
16

17 Catalyst Use and Contamination
18

19 The reforming catalysts regenerated by the process of the
20 present invention are used for aromatization of C_6 to C_{11} ,
21 preferably C_6 and C_7 non-aromatic hydrocarbons. Accordingly,
22 a hydrocarbon feedstream which comprises a C_6 to C_{11}
23 paraffin, olefin, or naphthene, is contacted with the
24 catalyst at aromatization conditions. Aromatization
25 conditions typically include an absolute pressure of from
26 about 0.5 to about 50.0 atmospheres, with the preferred
27 pressure being from about 1.0 to about 10.0 atmospheres, a
28 temperature of from about 800°F to about 1200°F, preferably
29 800°F to 1050°F, and a liquid hourly space velocity of from
30 between about 0.1 to about 10 per hour. Preferably,
31 hydrogen is employed in the process. When present, hydrogen
32 may be circulated at a rate of from about 1.0 to about 10.0
33 moles of hydrogen per mole of hydrocarbon in the hydrocarbon
34 feedstream. Feed streams entering the reforming reactors

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01 should be low enough in sulfur and water to prevent catalyst
02 deactivation by sulfur poisoning or platinum sintering.

03

04

Catalyst Regeneration Method

05

06 The gradual accumulation of coke and other deactivating
07 carbonaceous deposits on the catalyst will eventually reduce
08 the activity of the catalyst and selectivity of the
09 aromatization process. Typically, catalyst regeneration
10 becomes desirable when from about 0.5 to about 3.0 wt. % or
11 more of carbonaceous deposits are laid down upon the
12 catalyst. At this point, it is typically necessary to take
13 the hydrocarbon feedstream out of contact with the catalyst
14 and purge the hydrocarbon conversion zone with a suitable
15 gas stream. The catalyst regeneration method of the present
16 invention is then performed either by unloading the catalyst
17 from the conversion zone and regenerating in a separate
18 vessel or facility or performing regeneration in-situ.
19 Alternatively, the catalyst may be continuously withdrawn
20 from the reactor for regeneration in a separate vessel, to
21 be returned to the reactor as in a Continuous Catalytic
22 Reformer.

23

24 In fixed bed operation, it may sometimes be necessary to
25 dump the catalyst from the reactors and screen out fines in
26 order to reduce pressure drop. This typically occurs after
27 several years of operation. The dump and screen procedure
28 is usually done in combination with a catalyst regeneration.
29 First carbon is burned off the catalyst following the
30 procedures of this invention. This also serves to reoxidize
31 finely divided metals on the catalyst such as iron and
32 platinum. In their metallic form, these metals will rapidly
33 oxidize when exposed to air and possibly ignite a fire or
34 explosion when hydrocarbons are also present.

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01 The catalyst is then dumped from the reactors into a
02 screening device where the fines are removed. It is then
03 reloaded into the reactors and dried by circulating nitrogen
04 through the reactors and recycle gas dryer while heating to
05 reduction temperature. When water levels in the reactor
06 effluent are sufficiently low, the catalyst is then reduced
07 according the procedures of this invention and returned to
08 reforming service. The dryout time can be shortened and the
09 catalyst protected from water, carbon dioxide, and sulfur
10 compounds in the atmosphere by blanketing with nitrogen or
11 dry air during the dumping, screening, and reloading
12 processes.

13
14 According to the catalyst regeneration method of the present
15 invention, the essential step of the method incorporates a
16 lower temperature carbon burn step. The lower temperature
17 carbon burn step involves contacting the deactivated
18 catalyst with a gaseous mixture of oxygen and an inert gas.
19 The oxygen is typically derived from air and an inert gas
20 serves as a diluent, such that oxygen concentration is from
21 about 21 mole % oxygen to a lower limit which for the
22 practice of the present invention may be as low as
23 0.1 mole % oxygen. The practice of the present invention is
24 not limited to use of air, however, and higher levels of
25 oxygen may be used in methods where oxygen is supplied in a
26 more pure form such as from cylinders or other containing
27 means. Typical inert gases useful in the low temperature
28 carbon burn step may include nitrogen, helium, carbon
29 dioxide, and like gases or any mixture thereof; nitrogen
30 being preferred. The regeneration gases should be
31 substantially sulfur-free as they enter the reactor, and
32 preferably contain less than 100 part per million by volume
33 water. Because the oxygen content determines the rate of
34 burn, it is desirable to keep the oxygen content low so as

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01 not to damage the catalyst by overheating and causing metal
02 agglomeration, while still conducting the carbon burn step
03 in a manner that is both quick and effective. We have found
04 it desirable to keep the oxygen level in the inlet to the
05 regeneration vessel between 0.2 to 4.0 mole % during the
06 practice of the present invention to avoid thermal damage to
07 the catalyst, and still allow for the regeneration process
08 to be accomplished in a reasonable amount of time.

09
10 The low temperature carbon burn process of the present
11 regeneration method occurs at a temperature of between 300°F
12 to 780°F. Other conditions present during the low
13 temperature carbon burn step include a pressure sufficient
14 to maintain the flow of the gaseous oxygen containing
15 mixture through the catalyst zone such as a pressure of
16 between about 1.0 to 50.0 atmospheres and preferably from
17 about 2 to about 15 atmospheres, and a gas hourly space
18 velocity of about 100 to about 10,000 per hour, with a
19 preferred value of about 500 to about 5,000 per hour.

20
21 The regeneration method of the present invention is
22 performed in a halogen-free environment. By halogen-free,
23 we mean that chlorine, fluorine, bromine, or iodine or their
24 compounds including for example, hydrogen chloride, carbon
25 tetrachloride, ethylene dichloride, propylene dichloride;
26 are not added at anytime during the catalyst regeneration
27 process.

28
29 It is desirable to keep water levels low during the
30 reforming reactions and during the regeneration procedure.
31 This is especially true when temperatures are above 700°F.
32 Although short periods of time (several minutes) at water
33 levels as high as saturation can be tolerated at 700°F and
34 higher, it is desirable to avoid this high a water level.

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01 A preferred embodiment of the present invention includes the
02 use of a dryer in combination with flowing at least a
03 portion of the combustion gas resulting from the contacting
04 of the catalyst with the oxygen containing gas to a dryer
05 and recycling the dried combustion gas to the catalyst zone.
06 We have found that drying the recycle gas further reduces
07 catalytic metal agglomeration, resulting in a more active
08 regenerated catalyst. It is preferred that water in the
09 recycle gas be reduced to less than 1000 ppmv, more
10 preferably less than 10 ppmv, prior to the gas being
11 recirculated to the catalyst zone. We have found results to
12 be best when a fresh dryer is employed just prior to the
13 beginning of and throughout the coke-burn step.

14
15 In the preferred embodiment of the present invention, the
16 low temperature carbon burn step results in removing most of
17 the carbonaceous material from the catalyst while leaving an
18 amount of from between 0.1 to about 0.5 wt. % carbon on the
19 catalyst. Although the present invention is not limited by
20 any theory of operation, one possible explanation of the
21 resulting improved catalyst performance is that the small
22 amount of carbon remaining on the catalysts locates at the
23 acid sites, and thus significantly decreases the fouling
24 rate of the regenerated catalyst. Surprisingly, we have
25 also found the yield of C_3+ product to increase slightly
26 after a first regeneration of the catalyst.

27
28 Further, in another preferred embodiment of the present
29 invention, the first reactor inlet temperature is increased
30 during the carbon burn in a step-wise fashion over a period
31 of about one to five days from an initial temperature of
32 less than 500°F, preferably between 300°F and 500°F to
33 achieve a final peak catalyst bed temperature of less than
34 780°F, preferably between about 600°F and 750°F.

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01 The oxygen concentration at the first reactor inlet should
02 be controlled in the process of the present invention so as
03 to limit exotherms and high moisture levels due to
04 hydrocarbon combustion. Therefore, in the practice of a
05 preferred embodiment of the present invention, the oxygen is
06 maintained at a level between about 0.2 mole % and
07 2.0 mole % in the oxygen containing gas throughout the
08 carbon burn-off step. During the initial stages of the
09 burn, it is preferred the oxygen level be maintained at a
10 level between 0.2 and 0.5 mole %. As the rate of burn
11 subsides, oxygen levels may be increased to between 0.5 and
12 4.0 mole %.

13

14 The resulting regenerated catalyst with a portion of
15 carbonaceous material burned off is thereafter typically
16 cooled to about 500°F and purged with nitrogen or another
17 inert gas to displace the oxygen and any water therefrom.
18 The exit gas is easily monitored to determine when the
19 catalyst zone is substantially free of oxygen and water.

20

21 After the low temperature carbon burn-off and purge, the
22 catalyst is activated by treatment with hydrogen. In the
23 initial reduction step, the catalyst is contacted with a
24 hydrogen containing stream at a temperature of from about
25 300°F to about 700°F for a period of at least of about 0.1
26 to about 10.0 hours. Preferred conditions for the reduction
27 step are from about 400°F to about 600°F for a period from
28 about 0.1 to about 2.0 hours. The pressure and gas rates
29 utilized in the reduction step are preferably very similar
30 to those above described in the low temperature carbon burn
31 step. Following the initial reduction, the catalyst may be
32 further reduced and dried by circulating a mixture of inert
33 gas and hydrogen while raising the temperature to between
34 900 and 1000°F. In the reduction step, metallic components

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01 are returned to their elemental state and the resulting
02 regenerated catalyst possesses activity, and selectivity
03 characteristics quite similar to those occurring in a fresh
04 catalyst. Additionally, we have found the regenerated
05 catalyst has improved stability, as measured by a decreased
06 fouling rate. When iron oxides are present on the catalyst
07 or in the piping, it is desirable to use at least a 4:1 mole
08 ratio of nitrogen to hydrogen during the reduction and
09 dryout procedure, in order to limit the formation of NH_3 to
10 less than 200 ppmv.

11
12 After completing the reduction step, the temperature is
13 lowered to 800°F or less. The reforming process in which the
14 catalyst is employed may be resumed by charging the
15 hydrocarbon feedstream to the catalyst zone and adjusting
16 the reaction conditions to achieve the desired conversion
17 and product yields.

18
19 The following examples are intended to further exemplify the
20 invention, and are not intended to limit the invention in
21 any way.

22

23 LOW TEMPERATURE REGENERATION

24

25 EXAMPLE I

26

27 Pretreatment and Composition of Naphtha Feedstock

28

29 A hydrocarbon feedstock was hydrotreated and dried to remove
30 sulfur, oxygen, and water. The treated feed was stored
31 under nitrogen to keep it substantially free of water and
32 oxygen. The sulfur content of the hydrotreated feed was
33 about 0.1 ppmw. A gas chromatographic analysis showed the
34 following composition.

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		<u>LV%</u>
01		
02		
03	i-pentane	0.0
04	n-pentane	0.5
05	2,2-dimethylbutane	2.2
06	2,3-dimethylbutane	3.5
07	2-methylpentane	17.9
08	3-methylpentane	14.5
09	n-hexane	20.0
10	2,2-dimethylpentane	1.3
11	2,4-dimethylpentane	1.7
12	2,3-dimethylpentane	2.8
13	2-methylhexane	7.5
14	3-methylhexane	8.5
15	n-heptane	4.5
16	C ₈ ⁺ paraffins	2.1
17	cyclopentane	1.2
18	methylcyclopentane	4.9
19	cyclohexane	2.0
20	methylcyclohexane	0.5
21	other C ₆ - C ₇ naphthenes	1.7
22	benzene	0.2
23	toluene	0.7
24	ethylbenzene	0.2
25	heavies	1.6

EXAMPLE II

First Run Cycle Starting with Fresh Catalyst

Eighty cubic centimeters of fresh reforming catalyst were charged to a one-inch diameter tubular reactor. The catalyst comprised platinum on barium exchanged L-zeolite and a binder. The reactor was installed in a naphtha reforming pilot plant inside a three-zone electric furnace. Catalyst bed temperatures were measured by six equally spaced thermocouple points located from the top to the bottom of the catalyst bed in an axial thermowell. The

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01 pilot plant was purged and pressure tested with nitrogen,
02 depressured, then pressured to 100 psig with a blend of 1.0%
03 oxygen in nitrogen and the recycle compressor started. The
04 reactor effluent passed through a chilled liquid-gas
05 separator, a moisture analyzer, a dryer containing 4 A
06 molecular sieves, a compressor, a mass flowmeter, and back
07 to the reactor. The gas circulation rate was adjusted to
08 0.7 standard liters per minute. A small amount of the
09 recycle gas was allowed to bleed off the recycle loop and
10 makeup oxygen/nitrogen blend was fed from a cylinder.

11
12 The catalyst was dried by circulating the oxygen/nitrogen
13 blend and heating the to 500°F. The temperature was held at
14 500°F until the reactor effluent contained less than 300 ppm
15 water. The furnace temperature was then raised to 600°F and
16 held until water in the reactor effluent again was less than
17 300 ppm. Finally, the temperature was raised to 700°F and
18 held until the reactor effluent contained less than 100 ppm
19 water. The reactor was cooled to 500°F and the
20 oxygen/nitrogen makeup gas replaced with dry nitrogen. The
21 pilot plant was purged of oxygen and the pressure adjusted
22 to 70 psig with the compressor continuing to operate at the
23 same setting.

24
25 Catalyst reduction was initiated by switching the makeup gas
26 from nitrogen to hydrogen and pressuring from 70 psig up to
27 100 psig. The compressor setting was then readjusted to
28 again obtain a circulation rate of 0.7 standard liters per
29 minute. After holding at 500°F for an hour, the reactor
30 furnace reactor temperature was raised to 700°F at rate of
31 50°F/h. The temperature was held at 700°F until water in
32 the reactor effluent was less than 300 ppmv and then raised
33 to 800°F at 50°F/h. When moisture in the reactor effluent
34 again fell below 300 ppmv, the temperature was raised to

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01 900°F and held until water in the reactor effluent was less
02 than 100 ppmv. The furnace temperature was then lowered to
03 800°F and preparations were made for naphtha feed
04 introduction. This included putting a sulfur
05 converter/sorber reactor on-line in the recycle loop between
06 the naphtha feed introduction point and the reforming
07 reactor. The purpose of the sulfur converter/sorber was to
08 reduce sulfur compounds in the feed entering the reforming
09 reactor to below 5 ppbv.

10

11 The naphtha feed from Example I was fed at a rate of
12 128 mL/h corresponding to a liquid hourly space velocity
13 (LHSV) of 1.6 volumes of feed per volume of catalyst per
14 hour. Pressure was controlled at 100 psig by allowing
15 product hydrogen gas to exit the recycle loop through a back
16 pressure regulator. The product hydrogen stream was
17 analyzed and the hydrogen recycle rate was adjusted to
18 obtain a hydrogen to naphtha feed molar ratio of 3.0.
19 Liquid product was collected in the separator at 60°F. A
20 level control and valve allowed the separator to drain into
21 a debutanizer still which produced a C₃+ liquid product.

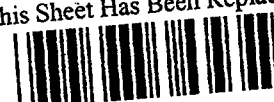
22

23 After feed introduction, the furnace temperature was rapidly
24 raised until the catalyst aromatization activity was able to
25 produce a liquid product comprising 42 wt. % aromatics. The
26 yield of liquid product was about 85 LV% on feed.
27 Thereafter as the catalyst deactivated temperatures were
28 raised to maintain constant aromatics in the liquid product.

29

30 In order to determine aromatization activity in terms of a
31 start-of-run temperature, the following procedure was used.
32 After an initial lineout period, the average catalyst bed
33 temperature was plotted against time to determine the
34 catalyst deactivation rate. Such plots are generally linear

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01 and may be fitted by the least squares method. The slope of
02 the line is the catalyst deactivation rate and the
03 start-of-run temperature is defined as the zero time
04 intercept. An approximate eventual run length is estimated
05 by making a linear extrapolation to the end of run
06 temperature. At end of run, aromatics selectivity begins to
07 decrease and catalyst deactivation accelerates markedly.
08 The end of run temperature was expected to be 935°F for the
09 feed and run conditions above.

10

11 After startup, the pilot plant ran at constant LHSV, recycle
12 ratio, pressure, and aromatics for 658 hours. A least
13 squares fit of the reaction temperature data yielded a
14 fouling rate of 0.026°F/h and a start-of-run temperature of
15 855°F. Assuming an end of run temperature of 935°F, the
16 eventual run length would have been about 3100 hours if the
17 reaction conditions had remained unchanged.

18

19 After 658 hours on-stream, reaction conditions were changed
20 in order to study process variable effects. The run
21 continued under various conditions for a total of
22 3810 hours. At the end of the run, the naphtha feed was
23 stopped and hydrogen circulation was continued while the
24 reactor furnace cooled to 500°F. The unit was then purged
25 with nitrogen and allowed to cool to ambient temperature.
26 Finally, the reactor was blocked off under nitrogen pressure
27 and the catalyst saved for a future regeneration.

28

29

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01

EXAMPLE III

02

03

First Regeneration of the Catalyst

04

05 The reactor containing the catalyst from Example II was
06 reinstalled in the pilot plant, purged with nitrogen, and
07 heated to reaction temperature in hydrogen. The reforming
08 reaction was then resumed at the original space velocity,
09 pressure, and recycle ratio to determine catalytic activity.
10 After 84 hours on stream it was determined that and an
11 average catalyst temperature of 919°F was required to make a
12 C₇+ liquid product containing 42 wt. % aromatics. The
13 catalyst had therefore aged 74°F since the start of run in
14 Example II.

15

16 Hydrogen circulation continued while the naphtha feed was
17 stopped and the reactor furnace was cooled to 500°F. At
18 500°F, the sulfur converter/sorber reactor was bypassed and
19 blocked-in and the separator drained. Recycle gas
20 circulation continued overnight while the recycle loop was
21 purged with nitrogen and the reforming reactor cooled to
22 300°F.

23

24 The carbon burn was initiated at 300°F and 95 psig by
25 introducing air and about sixty standard cubic centimeters
26 per minute of 1.0% oxygen/nitrogen blend to the recycle gas
27 stream and adjusting the air flow to maintain about 1.0%
28 oxygen in the gas entering the reforming reactor. The
29 recycle gas rate was 1.3 standard liters per minute. The
30 air was dried with molecular sieves and metered through a
31 mass flowmeter. The oxygen/nitrogen blend was added to
32 provide enough off-gas for oxygen analysis. The molecular
33 sieve dryer remained in the recycle loop and moisture levels
34 were measured before and after the dryer. Reactor inlet

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01 oxygen concentration was maintained at about 1.0% throughout
02 the burn. Water in the reactor inlet stream was less than
03 5 ppmv.

04

05 Upon introducing air an exotherm equal to about 20°F was
06 obtained at the front end of the catalyst bed. This was
07 attributed to the combustion of hydrocarbon vapors in the
08 recycle gas. The exotherm subsided after several hours.
09 The furnace temperature was held at 300°F for 22 hours then
10 raised to 500°F at a rate of 50°F/h. As the furnace
11 temperature was raised, the exotherm increased to about 25°F
12 and moved through the catalyst bed. The oxygen
13 concentration in the reactor effluent dropped to zero. By
14 the time the furnace temperature reached 500°F the exotherm
15 and oxygen consumption were decreasing again.

16

17 The furnace temperature was held at 500°F for 20.0 hours
18 then raised to 600°F at a rate of 50°F per hour. Again, the
19 burning of catalyst coke accelerated as temperature was
20 raised. The exotherm increased and oxygen in the reactor
21 effluent decreased. The exotherm peaked at about 10°F and
22 oxygen conversion peaked at about 30%. A short time after
23 the furnace temperature reached 600°F, the burning again
24 subsided.

25

26 After holding at 600°F for 22.0 hours, the furnace
27 temperature was raised 50°F/h to 700°F. This time the peak
28 exotherm was less than 5°F. After 22.0 hours at 700°F, the
29 air and oxygen/nitrogen blend were shut-off. The recycle
30 gas dryer which was now loaded with water and carbon dioxide
31 was bypassed and a fresh dryer brought on-line. Gas
32 circulation continued while the recycle loop was purged with
33 nitrogen and the reforming reactor was cooled to 500°F.

34

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01 Catalyst reduction was initiated at 500°F by depressuring to
02 70 psig and then pressuring up to 100 psig with hydrogen
03 while the compressor continued to operate. The makeup gas
04 was switched from nitrogen to hydrogen. The temperature was
05 held at 500°F for one-hour and then raised 4°F/h to 900°F.
06 The temperature was held at 900°F for 16 hours before
07 cooling to 800°F for naphtha feed introduction.

08

09

EXAMPLE IV

10

11

Catalyst Performance After First Regeneration

12

13 After catalyst regeneration, the naphtha reforming reaction
14 was resumed with the same conditions and feed used in
15 Example II. Liquid product yields were the same as before
16 regeneration and slightly better than with fresh catalyst.
17 After 840 h on stream a least squares fit was made as before
18 to determine the start-of-run temperature and deactivation
19 rate. The start-of-run temperature was 859°F and the
20 catalyst deactivation rate was 0.017°F/h. Thus, the
21 catalyst activity had been restored to within 4°F of fresh
22 catalyst. Surprisingly, the catalyst deactivation rate was
23 significantly less than with fresh catalyst. The projected
24 run length was 4300 hours compared to 3100 hours for the
25 first cycle.

26

27 After determining start-of-run temperature and catalyst
28 deactivation rate, the liquid hourly space was increased to
29 3.0 and the furnace temperature was increased to obtain a
30 maximum catalyst bed temperature of 1025°F in order to
31 accelerate catalyst fouling. After 1464 hours at these
32 conditions, the catalyst had reached approximately end of
33 run activity and the liquid hourly space velocity was
34 reduced to the original value of 1.6. The average catalyst

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01 bed temperature to produce a liquid product containing
02 42 wt. % aromatics was then determined to be 939°F. The
03 catalyst had aged 80°F from the start of the second run
04 cycle.

05

06

EXAMPLE V

07

08

Second Regeneration of the Catalyst

09

10 At the conclusion of the run cycle described in Example IV,
11 the naphtha feed was stopped and the reforming reactor was
12 cooled to 500°F while continuing to circulate hydrogen. At
13 500°F, the recycle loop was purged with nitrogen, the sulfur
14 converter/sorber was taken off-line, and the separator was
15 drained. Purging continued while the reactor cooled to
16 300°F.

17

18 The catalyst was then regenerated following substantially
19 the same procedure used in Example III.

20

21

EXAMPLE VI

22

Catalyst Performance Following Second Catalyst Regeneration

23

24
25 After the second regeneration, the reforming reaction was
26 restarted with same conditions and feed used at the start of
27 the first and second run cycles. After 660 hours, a least
28 squares fit was again made to determine the start-of-run
29 temperature and catalyst deactivation rate. The
30 start-of-run temperature was determined to be 874°F and the
31 catalyst deactivation rate was 0.012°F/h. The projected run
32 length at these conditions was therefore about 5000 hours.
33 The start-of-run temperature had declined 13°F from the
34 start of previous run cycle, but the catalyst deactivation

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01 rate was again reduced so that projected run length had
02 increased. The liquid C₃* yield was the same as after the
03 first regeneration.

04

05

EXAMPLE VII

06

07

Regeneration without Dryer

08

09 A coked catalyst from a 4700 hour pilot plant run was saved
10 and later returned to service at the same conditions used in
11 the previous examples. Prior to its use, the catalyst had
12 the same composition as the catalyst used in Example II.
13 After 330 hours on-stream, the average catalyst bed
14 temperature was 930°F and liquid product contained 42 wt. %
15 aromatics. The yield of liquid product on feed was
16 beginning to decline and was 85.5 LV%.

17

18 At this point the naphtha feed was stopped and the reactor
19 cooled to 500°F in circulating hydrogen. At 500°F, the
20 recycle loop was purged with nitrogen and the sulfur
21 converter/sorber reactor and recycle gas dryer were bypassed
22 and the separator was drained. The pressure was adjusted to
23 85 psig. This time the carbon burn was started at 500°F.
24 Air and oxygen/nitrogen blend were added to the recycle gas
25 stream as in Examples III and V, but the oxygen content at
26 the reactor inlet was adjusted to 0.5% instead of 1.0%. The
27 dryer remained bypassed throughout the burn. There was
28 complete oxygen conversion and the exotherm was about 12°F.
29 After holding at 500°F for 1.5 hours, the furnace
30 temperature was raised 25°F/h to 700°F. Oxygen breakthrough
31 occurred when the furnace temperature reached about 640°F.
32 There was only a small amount of burning by the time the
33 furnace temperature reached 700°F and the exotherm was
34 negligible. Reactor inlet oxygen level was raised to 1.0%

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01 and the temperature held at 700°F for 20 hours to complete
02 the burn. The exotherm during the final burn was less than
03 2°F.

04

05 Since the recycle gas dryer was bypassed, water built up in
06 the recycle gas during the burn until it reached saturation
07 levels in the separator. Moisture levels in the recycle gas
08 exceeded 2000 ppm well into the 700°F hold period.

09

10 After completing the carbon burn, the recycle loop was
11 purged with nitrogen and the reactor was cooled to 500°F
12 while recycle gas circulation continued. At 500°F the dryer
13 and the sulfur converter/sorber were put back on line. When
14 water in the recycle gas fell below 100 ppmv, the plant was
15 pressured up 100 psig with hydrogen to initiate catalyst
16 reduction. After an hour at 500°F, the reactor was heated
17 to 900°F at rate of 10°F/h. The reactor was held at 900°F
18 until the moisture content of the reactor effluent was less
19 than 100 ppm then cooled to 800°F for feed introduction.

20

21

EXAMPLE VIII

22

Catalyst Performance after Regenerating without a Dryer

23

24
25 After the catalyst regeneration in Example VII, the naphtha
26 feed was restarted and the reforming reaction resumed for
27 590 hours. The feed and the run conditions were the same as
28 in Example II. Catalyst performance was not as good as
29 obtained in Examples II, IV, or VI. The start-of-run
30 temperature was 868°F and the fouling rate was 0.031°F/h.
31 The projected run length was therefore only about
32 2100 hours.

33

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EXAMPLE IX

Regeneration with Dryer

The regeneration procedure of Example VIII was repeated with another coked catalyst sample except that the recycle gas dryer was employed during the carbon burn and consequently the reactor inlet moisture levels were always less than 5 ppm. The catalyst composition prior to its use as a reforming catalyst was the same as that used in Examples II and VII.

EXAMPLE X

Catalyst Performance After Regeneration with Dryer

The catalyst regenerated in Example IX was tested with the same run conditions and feed as in Example VIII. After 576 hours on-stream, the start-of-run temperature was 862°F and catalyst deactivation rate was 0.019°F/hr. The projected run length was 3800 hours compared to 2100 in Example VIII.

The results of from Examples I to X are summarized in Table 1 below.

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TABLE 1

<u>Description</u>	<u>Examples</u>	<u>Start of Run Temp. °F</u>	<u>Deactivation Rate °F/h</u>	<u>Projected Run(hours)</u>
Fresh Catalyst	II	855	0.026	3100
First Regeneration	II-IV	859	0.017	4100
Second Regeneration	V-VI	874	0.012	5000
Regeneration without Dryer	VII-VIII	868	0.031	2100
Regeneration with Dryer	IX-X	862	0.019	3800

The Table clearly shows that a controlled low temperature carbon-burn regeneration procedure restores most of the activity present at the start of the previous run cycle and that catalyst deactivation rates are significantly reduced, such that several cycles are possible before there is a need for platinum redispersion. The results further show the advantage in using a dryer to reduce the water content of the recycle gas during the carbon burn. These results are surprising in view of the prior art and afford the opportunity to increase cycle length and avoid the use of corrosive and sometimes highly toxic halogen compounds during regeneration.

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EXAMPLE XI

Regeneration Procedure for a Large-Scale Plant

01
02
03
04
05 Allowing for differences in the exotherm as compared to a
06 pilot plant, a commercial unit with four reactors in series
07 is regenerated as follows. Naphtha feed is withdrawn and
08 hydrogen is circulated at high temperature to strip
09 hydrocarbon from the catalyst. The separator and knockout
10 drums are periodically drained of hydrocarbon. Hydrogen
11 circulation is continued while the reactors are cooled to
12 about 420°F. At 420°F, the recycle loop is purged with
13 nitrogen and low points are checked for liquid hydrocarbons.
14 After periodic draining shows that little or no hydrocarbon
15 liquids are being collected, it is advantageous to switch to
16 a fresh recycle gas dryer which is substantially free of
17 hydrocarbons and water. If there is a recycle gas sulfur
18 converter/sorber, it will be bypassed at this point.
19
20 When the reactor inlets are at 420°F and the level of
21 combustibles in the recycle gas is less than 2.0%, air is
22 introduced to the recycle gas stream. The oxygen level at
23 the first reactor inlet is adjusted to 0.5%. The burning of
24 residual combustibles in the recycle gas consumes all the
25 oxygen and results in an 80 to 125°F exotherm across the
26 first reactor. Eventually, the vapor-phase combustibles are
27 consumed and the burn-wave moves through the reactor chain.
28 After oxygen breakthrough occurs and the exotherm subsides,
29 furnace temperatures are raised at rate of about 25°F/h
30 until peak catalyst bed temperature reaches 700°F. The
31 total exotherm at this point is less than about 20°F. When
32 oxygen conversion across the reactor train drops to less
33 than 10%, the oxygen concentration at the reactor inlet is
34 raised to 1.0 to 4.0% and the furnace temperatures are

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01 adjusted to maintain the peak catalyst bed temperatures as
02 close to 700°F as possible.
03
04 Temperatures are maintained at 700°F for 12 to 24 hours
05 before the air makeup is stopped. The recycle loop is then
06 purged with nitrogen and cooled to 500°F. At 500°F the
07 recycle gas dryers are switched again and the sulfur
08 converter/sorber is brought back on-line. About twice the
09 stoichiometric amount of hydrogen needed for reduction of
10 the catalyst is fed into the unit over a period of about an
11 hour. The unit is then partially depressured and pressured
12 up with hydrogen to adjust the hydrogen to nitrogen ratio to
13 about one-to-four. Higher hydrogen to nitrogen ratios can
14 result in excessive ammonia formation, which is catalyzed by
15 the iron particles present in the reactor tubes. The
16 temperature is held at 500°F for about an hour then raised
17 10°F/h to 900°F. The hydrogen/nitrogen ratio is maintained
18 by adjusting hydrogen and nitrogen makeup rates. The
19 temperature is held at 900°F for at least 12 hours. When
20 water in the fourth reactor effluent is less than 100 ppm,
21 the temperature is dropped to 700°F or lower to await feed
22 introduction.
23

24 EXAMPLE XII

25
26 Reforming With A Silicalite Catalyst/Catalyst Coking
27

28 A silicalite catalyst was produced by impregnating a dried
29 synthesized Silicalite powder to give 1% Pt on the
30 Silicalite powder, then mixing this with SAPO-11 powder to
31 produce a finished catalyst consisting of 25% wt SAPO-11 and
32 75% wt Pt Silicalite.
33
34

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01 This catalyst was used to convert hexane containing feeds to
02 aromatics. The feed compositions are listed in Table 3.
03 The conversion conditions used were a pressure of 30 psig, a
04 WHSV of 0.72, a hydrogen to hydrocarbon ratio of seven to
05 one, with the catalyst temperatures ranging from 880 to
06 1000°F to maintain a high product benzene level and adjust
07 for fouling.

08

09

EXAMPLE XIII

10

11

Regeneration Of Silicalite Catalyst

12

13 The catalyst of Example XII was repeatedly coked and
14 regenerated. The regeneration conditions included treating
15 the catalyst with low concentrations (0.5 to 2.0 wt. %) of
16 oxygen at 30 to 100 psig at a GHSV of 923. During
17 regeneration, the regeneration gases contained less than
18 100 ppm water.

19

20 The regeneration temperature was varied over the range of
21 450 to 680°F. Regenerations below about 500°F for 16 to
22 24 hours were not successful in producing a catalyst having
23 an activity (as measured by hexane conversion) or a
24 selectivity (as measured by the wt. % benzene in the
25 product) similar to fresh catalyst. At regeneration
26 temperatures between 550 and 680°F, aromatization activity
27 was restored to about that of the start of the run cycle.

28

29 Table 2, below, shows the regeneration temperatures and
30 times for several of these regenerations, along with the
31 activity and selectivity results. The regenerated catalyst
32 was able to maintain product benzene levels of about
33 40 wt. %, for greater than 1000 hours between regenerations.

34

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REGENERATION CONDITIONS				SELECTIVITY AND ACTIVITY RESULTS*					
Regen. No.	Temp. °F	Hours	O ₂ Level %	Pressure Psig	Before Regen.		After Regen.		Hours on Stream ^{4,24} Producing BZ
					Hexane Conv.	Product Wt. % BZ	Hexane Conv.	Product Wt. % BZ	
10	600	72.0	0.5	30	55	14	74	41	1200
	630	46.7	1.0	100					
11	600	46.8	1.0	100	82	27	68	39	1200
	630	3.6	1.0	100					
12	600	26.3	1.0	100	86	8	72	41	1700
	630	65.3	1.0	100					
	660	119.2	1.0	100					
13	600	56.6	1.0	100	59	24	98	39	1000+ ⁴⁵
	630	24.9	1.0	100					
	660	30.9	1.0	100					
	680	43.9	1.0	100					
0	Fresh Catalyst at 21 Hrs. on Stream				98 ⁴⁴	42 ⁴⁵			
*Conversion Conditions: 30 psig, WHSV = 0.72, Catalyst Temp. 880°F to 1000°F									
**Utilizing Feed B (Table 3)									
***At constant (40%) aromatization activity.									
****Utilizing Feed A (Table 3)									
*****BZ = Benzene									
****Run was voluntarily terminated; catalyst remained active.									

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01

TABLE 3

02

03

FEED COMPOSITION

04

05

FEED A

FEED B

06

LIGHT NAPHTHA

MODEL FEED

07

08

COMPOUND

wt. %

wt. %

09

10

Total C₃

16.1

0.0

11

Total C₄

49.7

70.0

12

13

Total C₇

34.2

24.0

14

N-C₆

12.5

70.0

15

16

Methyl
Cyclohexane

5.9

6.0

17

18

19

Feed A used for start of run.

20

Feed B used for regeneration studies.

21

22

EXAMPLE XIV

23

24

Effect of Raising Temperature After

25

Substantially Completing Carbon Burn at Low Temperatures

26

27

This example shows that temperature may be raised beyond the

28

780°F limit after substantially completing a halogen-free

29

carbon burn regeneration at lower temperatures. A platinum

30

on barium exchanged L-zeolite catalyst was used to reform a

31

light naphtha feedstock very similar to the one shown in

32

Table 1 of the specification. At the end of the run, the

33

catalyst was regenerated as follows.

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01 The naphtha feed was stopped. The reactor was cooled to
02 500°F while adding makeup hydrogen. After reaching 500°F,
03 the unit was purged with nitrogen gas to remove
04 substantially all of the hydrogen. Any remaining liquid
05 hydrocarbons were drained from the gas liquid separator and
06 other low points in the system. The nitrogen makeup rate
07 was then reduced to a low level, the sulfur converter/sorber
08 was by-passed, and the pressure and recycle gas rate were
09 adjusted to about 85 psig and 1000 GHSV, respectively.

10

11 After purging the recycle loop with nitrogen, air was added
12 through a mass flowmeter to bring the reactor inlet oxygen
13 concentration to 0.5%. After holding for two hours at
14 500°F, the temperature was raised 25°F/h to 760°F while the
15 inlet oxygen level was maintained between 0.4 and 0.6%. The
16 temperature was then held overnight at 760°F with the inlet
17 oxygen level between 1.0 and 1.3%.

18

19 After 16 hours at 760°F, the carbon burn was substantially
20 complete as indicated by the difference between inlet and
21 oxygen concentrations which was less than 0.05%. The
22 temperature was then raised to 850°F and maintained at 850°F
23 for 14 hours. A small amount of additional burning occurred
24 at the high temperature but at a very low rate.

25

26 The reactor was then purged with nitrogen and a fresh
27 recycle gas dryer brought on-line while the reactor cooled
28 to 500°F. When the water level in the reactor effluent was
29 less than 100 ppm, catalyst reduction was initiated by
30 pressuring from 85 to 100 psig with hydrogen. The nitrogen
31 makeup gas was stopped and pressure was maintained at
32 100 psig by adding hydrogen makeup gas. The temperature was
33 held at 500°F for two hours and then raised 10°F/h to 900°F.

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01 Feed was reintroduced and the reforming reaction was resumed
02 at the same conditions used in our previous examples and
03 temperature was adjusted to maintain 42 wt. % aromatics in
04 the liquid product. After 1070 hours on-stream, a
05 least-squares plot was made of the data from 186 to
06 1070 hours. From this plot, it was determined that the
07 start-of-run temperature was 868°F/h and the fouling rate
08 was 0.020°F/h, which compares to 850°F and 0.026°F/h,
09 respectively, for fresh catalyst. The projected run length
10 was 3350 hours compared to 3300 for fresh catalyst. The
11 regeneration was not as good as those of the previous
12 examples where temperature was kept below 780°F but was
13 considered acceptable.

14

15

16 As can be seen by this Example, there was no improvement in
17 catalyst performance obtained by raising temperature of the
18 oxygen after substantially completing the carbon burn at a
19 temperature below 780°F.

20

21

EXAMPLE XV

22

Regeneration with up to 520 ppm Water in the Recycle Gas

24

25 This experiment shows that up to 520 ppm water can be
26 present in the recycle gas and still achieve an acceptable
27 regeneration. It is, therefore, possible although not
28 preferred to use wet air for the regeneration. Also, one
29 may consider using a less expensive dessicant than molecular
30 sieves in the recycle gas dryer, such as silica-gel or
31 activated alumina.

32

33 The catalyst from Example II was regenerated a second time
34 as follows. Preparations for the carbon burn were the same

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01 as above. Before adding air, water was added to the recycle
02 gas stream by bubbling makeup nitrogen through water
03 contained in a small bomb. The makeup nitrogen feed rate
04 was adjusted to obtain about 500 ppmv water in the gas
05 stream entering the reactor and air was added to bring the
06 oxygen level to 0.5%. During the carbon burn, the reactor
07 inlet oxygen level was maintained between 0.4 and 0.6 and
08 the inlet water level between 420 and 520 ppmv by adjusting
09 the air and nitrogen feed rates.

10

11 After holding for two hours at 500°F, the temperature was
12 raised 25°F/h to 700°F while maintaining inlet oxygen levels
13 between 0.4% and 0.7%. The temperature was then held
14 20 hours at 700°F with the inlet oxygen level rising from
15 0.6 and 1.2%. The air was then shut off and dry makeup
16 nitrogen was substituted for water-saturated nitrogen. A
17 fresh dryer was put on-line and the reactor was cooled to
18 500°F.

19

20 When the water level in the reactor effluent was less than
21 100 ppm, the catalyst was reduced and the reforming reaction
22 resumed as in the previous example. After 600 hours
23 on-stream, the start-of-run temperature and fouling rate
24 were calculated to be 875°F and 0.0186°F, respectively.
25 This corresponds to a projected run length of 3225 hours,
26 which is close to that of fresh catalyst.

27

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01 WHAT IS CLAIMED IS:

02

03 1. A process for regenerating a coke-contaminated
04 reforming catalyst comprising platinum on a molecular
05 sieve, said process comprising of:

06

07 (a) contacting said catalyst in a catalyst zone with a
08 halogen-free oxygen-containing gas at a
09 temperature of less than 780°F, said gas having a
10 water content of less than about 1000 ppmv; and

11

12 (b) oxidizing at least a portion of said coke to
13 produce a combustion gas for a sufficient period
14 of time such that the catalyst aromatization
15 activity is restored to within 20°F of the
16 activity said catalyst possessed at the start of
17 the previous run cycle.

18

19 2. A process for regenerating a coke-contaminated
20 reforming catalyst comprising platinum on a molecular
21 sieve, said process comprising of:

22

23 (a) contacting said catalyst in a catalyst zone with a
24 halogen-free oxygen-containing gas at a
25 temperature of less than 780°F, said gas having a
26 water content of less than about 1000 ppmv;

27

28 (b) oxidizing at least a portion of said coke to
29 produce a combustion gas for a sufficient period
30 of time such that the catalyst aromatization
31 activity is restored to within 20°F of the
32 activity said catalyst possessed at the start of
33 the previous run cycle;

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- 01 (c) passing at least a portion of said combustion gas
02 through a dryer to produce a dried gas having a
03 water content less than said portion of combustion
04 gas; and
05
06 (d) recycling at least a portion of said dried gas to
07 said catalyst zone.
08
09 3. A process for regenerating a coke-contaminated
10 reforming catalyst comprising platinum on a molecular
11 sieve, said process comprising of:
12
13 (a) contacting said catalyst in a catalyst zone with a
14 halogen-free oxygen-containing gas at a
15 temperature of less than 780°F, said gas having a
16 water content of less than about 1000 ppmv;
17
18 (b) oxidizing at least a portion of said coke to
19 produce a combustion gas for a sufficient period
20 of time such that the catalyst aromatization
21 activity is restored to within 20°F of the
22 activity said catalyst possessed at the start of
23 the previous run cycle;
24
25 (c) passing at least a portion of said combustion gas
26 through a dryer to produce a dried gas having a
27 water content less than said portion of combustion
28 gas;
29
30 (d) recycling at least a portion of said dried gas to
31 said catalyst zone; and
32
33 (e) reducing the regenerated catalyst by contacting
34 the catalyst with a gaseous stream containing

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- 01 hydrogen at an initial temperature from 300°F to
02 700°F.
03
- 04 4. The process as recited in Claim 1, 2 or 3 wherein the
05 oxygen content of the oxygen containing gas is from
06 between about 0.1 to about 21.0 mole % oxygen.
07
- 08 5. The process as recited in Claim 1, 2 or 3 wherein the
09 oxygen content of the oxygen containing gas is from
10 about 0.2 to about 4.0 mole %.
11
- 12 6. The process as recited in Claim 1, 2 or 3 wherein the
13 molecular sieve is a large-pore zeolite.
14
- 15 7. The process as recited in Claim 6 wherein the
16 large-pore zeolite is selected from the group
17 consisting of type-X, type-Y, beta zeolite, and
18 mordenite.
19
- 20 8. The process as recited in Claim 6 wherein the
21 large-pore zeolite is type-L zeolite.
22
- 23 9. The process as recited in Claim 1, 2 or 3 wherein the
24 molecular sieve is silicalite.
25
- 26 10. The process as recited in Claim 6 wherein the zeolite
27 further comprises an alkaline earth metal.
28
- 29 11. The process as recited in Claim 6 wherein the zeolite
30 further comprises boron.
31
- 32 12. The process as recited in Claim 1, 2 or 3 wherein said
33 catalyst is bound with a support matrix comprising
34 alumina, silica or mixtures thereof.

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- 01 13. The process as recited in Claim 3 further comprising
02 raising the temperature of the gaseous stream
03 containing hydrogen to between 800°F and 1000°F to
04 complete the dryout and reduction.
05
- 06 14. The process as recited in Claim 3 wherein the carbon
07 burn is initiated at a temperature of less than 500°F.
08
- 09 15. The process as recited in Claim 14 wherein the
10 temperature is escalated during the carbon burn in a
11 slow ramping fashion.
12
- 13 16. The process as recited in Claim 14 wherein the
14 temperature is escalated during the carbon burn in a
15 stepwise fashion.
16
- 17 17. The process as recited in Claim 1, 2 or 3 wherein the
18 peak catalyst temperature during the carbon burn step
19 is between 600°F and 750°F.
20
- 21 18. The process as recited in Claim 3 wherein prior to
22 reducing the catalyst, the catalyst is purged with an
23 inert gaseous stream.
24
- 25 19. The process as recited in Claim 3 further comprising:
26
- 27 (a) passing at least a portion of said gaseous stream
28 containing hydrogen through a dryer; and
29
- 30 (b) recycling a portion of said gaseous stream
31 containing hydrogen to said catalyst zone.
32
- 33 20. The process as recited in Claim 3 further comprising
34 reducing the regenerated catalyst by contacting the

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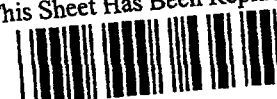


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- 01 catalyst with a gaseous stream containing a mixture of
02 inert gas and hydrogen at a temperature between 900°F
03 and 1000°F.
04
- 05 21. The process as recited in Claim 3 further comprising
06 reducing the regenerated catalyst by contacting the
07 catalyst with a gaseous stream containing a mixture of
08 nitrogen and hydrogen at a temperature between 900°F
09 and 1000°F.
10
- 11 22. The process as recited in Claim 21 wherein the mole
12 ratio of nitrogen gas to hydrogen gas is at least 4:1.
13
- 14 23. A process for regenerating a coke deactivated reforming
15 catalyst, comprising:
16
- 17 (a) contacting a coke-contaminated L-zeolite catalyst
18 with a halogen-free oxygen-containing gas at a
19 temperature of less than 780°F, said gas having a
20 water content between 100 and 1000 ppmv;
21
- 22 (b) oxidizing at least a portion of said coke to
23 produce a combustion gas for a sufficient period
24 of time such that the aromatization activity of
25 the L-zeolite catalyst is restored within 20°F of
26 the activity said catalyst possessed at the start
27 of the previous run cycle;
28
- 29 (c) passing at least a portion of said combustion gas
30 through a dryer to produce a dried gas having a
31 water content less than said portion of combustion
32 gas;
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- 01 (d) recycling at least a portion of said dried gas to
02 said catalyst zone; and
03
04 (e) reducing the regenerated catalyst by contacting
05 the catalyst with a gaseous stream containing
06 hydrogen at an initial temperature from 300°F to
07 700°F.
08
09 24. The process as recited in Claim 23 further comprising
10 the step of purging the catalyst resulting from step
11 (b) with a gaseous stream comprising nitrogen prior to
12 the reduction step (c).
13
14 25. The process as recited in Claim 23 further comprising
15 the step of purging the catalyst resulting from
16 step (b) with a gaseous stream comprising nitrogen
17 prior to the reduction step (c) and changing the
18 recycle gas dryer so as to reduce carbon dioxide in the
19 recycle gas to less than 100 ppm.
20
21 26. The process as recited in Claim 23 wherein the
22 L-zeolite catalyst contains barium.
23
24 27. A reforming process wherein a reforming catalyst is
25 regenerated for at least two cycles by the process as
26 recited in Claim 1, 2, 3 or 23.
27
28 28. The process as recited in Claim 1, 2, 3 or 23 wherein
29 the catalyst is continuously withdrawn from reactors
30 for regeneration in a separate vessel, and returned to
31 the reactors.
32
33 29. A reforming process comprising contacting a hydrocarbon
34 feed with a platinum containing molecular sieve

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01 catalyst under reforming conditions and regenerating
02 said catalyst in accordance with the process of
03 Claim 1, 2 or 3.
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ABSTRACT OF THE INVENTION

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A process for regenerating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780°F for a sufficient period of time such that the aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle.

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REPLACED SHEETS		SG
☒	Description : paged1... to paged41....	
☒	Claim(s) : paged42... to paged48....	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
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REPLACEMENT SHEETS		SG
☒	Description : paged1... to paged41....	
☒	Claim(s) : paged42... to paged48....	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
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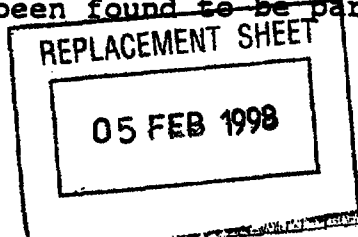
LOW TEMPERATURE REGENERATION OF COKE DEACTIVATED REFORMING CATALYSTS

BACKGROUND OF THE INVENTION

The subject of the present invention is a process for the regeneration of a hydrocarbon reforming catalyst which has been deactivated due to buildup of carbonaceous material on the catalyst. More specifically, the present invention provides a method for regenerating a coke deactivated reforming catalyst by a controlled low temperature carbon-burn procedure which results in the catalyst having activity, selectivity and stability characteristics approximating, or which are even better than, the catalyst prior to the buildup of carbon. The reforming catalysts intended to be regenerated by the process of the present invention comprise a molecular sieve material and platinum.

Platinum containing catalysts are widely used in the oil refining and petrochemical industries, and are particularly important in a reforming process where paraffins, olefins and naphthenes are converted to aromatic compounds. Conventional reforming catalysts typically include one or more metals, most typically platinum, dispersed on a base, and may also include a binding agent for adding physical support to the base, and chloride to provide an acidic function. Typically, the catalyst base is alumina, but recently molecular sieve based catalysts have been found to be effective for reforming reactions.

Catalytic compositions containing zeolites are well known in the industry and recently the use of L-zeolites in combination with other specified catalytic components have been found to be particularly preferred for reforming. The



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aromatic compounds produced by such a catalytic conversion are valuable to a refiner due to their higher octane rating, and may be recovered from the reforming product for further processing and reaction in the petrochemical industries. The L-zeolite catalysts are particularly effective for converting C₆ and C₇ non-aromatic hydrocarbons which normally boil between 125°F and 225°F, to benzene and toluene.

In the reforming process, a hydrocarbon feedstock is passed through a catalyst-containing reactor in the presence of hydrogen at an elevated temperature. In the reactor and upon contact with the reduced or activated catalyst, some of the paraffins, olefins and naphthenes in the feedstock react to form a more desired, higher octane aromatic product. In the course of typical reforming operations, the catalysts will typically become deactivated due to the deposition of carbonaceous material or "coke" upon the catalyst, and/or sintering or poisoning of the catalytic metal particles. In commercial practice, the deactivated catalyst will then be regenerated by a process which may include as a step the exposing of the catalyst to an oxygen containing gas at elevated temperature (typically 950°F final burn temperature) to burn the carbonaceous deposits accumulated on the catalyst. However, prior to our present invention, burning the coke off the catalyst at elevated temperatures caused the catalytic metal to agglomerate, which significantly lowered the activity and thus worsened the performance of the catalyst. Consequently, specific steps directed to the redispersion of the catalytic metal on the base were necessary. The redispersion steps typically comprise contacting the catalyst with a chloride containing gas in the presence of oxygen and water vapor, and are well known in the art.

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In U.S. Patent No. 4,493,901 issued January 15, 1985 to Bernard et al., a method of regenerating a catalyst comprising platinum and a non-acidic L-zeolite is described, whereby the catalyst is subjected to a multi-step process, the first step being exposure to a hydrogen environment, followed by a carbon burn step, and then a calcination step followed specifically by an oxychlorination step. The regeneration method of Bernard et al. utilizes a hydration step following the oxychlorination step. In the hydration step, a quantity of water is added to the cooling air.

In U.S. Patent No. 4,810,683, issued March 7, 1989, to Cohn, a method is described which utilizes a halogen or halogen containing gas during the carbon burn step. The burning step of the process of U.S. Patent No. 4,810,683 occurred necessarily in the presence of a halogen or halogen containing gas and at a temperature of from 300°C to 600°C.

U.S. Patent No. 3,986,982, issued October 19, 1976, to Crowson et al., describes a method for regenerating a deactivated platinum group metal-loaded zeolites by burning off deposits on the catalyst with a stream of inert gas and oxygen at a temperature controlled to a maximum of 550°C. Example 1 shows a stepwise burn procedure to 530°C. The water content was held at 100-130 ppm. This was followed by treating with a stream of an inert gas containing from 0.5 to 20.0 vol% oxygen and from 5 to 500 ppmv chlorine as chlorine gas. The resultant catalyst is purged to remove residual oxygen and chlorine and then reduced with hydrogen.

U.S. Patent No. 4,359,400, issued November 16, 1982, to G. R. Landolt et al., describes a process whereby multimetallic platinum containing catalysts are contacted with oxygen containing gas at elevated temperatures to burn

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off coke and then treated with dry, oxygen-free hydrogen halide. The catalyst is then treated with Cl_2 containing gas which is oxygen and water-free.

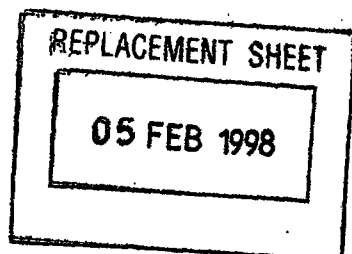
U.S. Patent Number 4,719,189, issued January 12, 1988 to A. S. Krishnamurthy describes a process for rejuvenating a coke-deactivated noble metal containing zeolite catalyst. The process comprises contacting the catalyst with a mixture of oxygen and sulfur dioxide, followed by catalyst reduction. Temperatures from 752-840°F are preferred.

U.S. Patent No. 4,645,751, issued February 24, 1987, to S. B. McCullen et al., describes a process for rejuvenating a highly silicious (silica-alumina ratio of at least 20) Pt zeolite catalyst wherein the Pt has become agglomerated. The agglomerated catalyst is first reduced with hydrogen. Following reduction the catalyst is treated with hydrogen chloride and oxygen in an inert gas carrier at 400-450°C.

U.S. Patent No. 4,752,595, issued June 21, 1988, to S. B. McCullen et al., describes a process for regenerating a noble-metal containing zeolite catalyst. The process consists of a coke burn step followed by a low temperature reduction step (212-482°F). Oxidizing conditions for the coke burn include temperatures ranging from 392-1004°F, preferably 752-950°F.

U.S. Patent No. 4,657,874, issued April 14, 1987, to W. S. Borghard et al., describes a method where Pt on a highly silicious zeolite is redispersed. The process comprises a coke burn followed by oxychlorination. The oxygen burn step is done under conditions that are sufficiently mild to prevent any alteration in the crystal structure of the zeolite. Example 6 uses a temperature of





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850°F. This is then followed by treating with a stream of inert gas containing 6 to 15 Torr of chlorine gas and water vapor such the molar ratio of water to chlorine gas is between 0.01 and 2.0. Oxygen may also be present. The rejuvenation is typically carried out at 450°C (842°F).

U.S. Patent No. 4,851,380, issued July 25, 1989, to D. A. Van Leirsburg et al., describes a process for regenerating a sulfur contaminated reforming catalyst. The process includes a platinum agglomeration step which can be accomplished by contacting the catalyst with O₂ between 800°F and 1200°F and an oxychlorination step. Pt redispersion by contacting an agglomerated catalyst with carbon monoxide and a sulfur free halogen acid gas.

U.S. Patent No. 4,855,269, issued August 8, 1989, to D. H. Mohr, discloses a platinum redispersion method comprising a wet oxychlorination step, followed by a nitrogen purge, followed by reduction.

U.S. Patent No. 4,914,068 issued April 3, 1990, to V. R. Cross, describes a process for the improved retention of the platinum dispersion following oxychlorination if the catalyst is cooled to 430°C or preferably less than 375°C prior to start of reduction. Coke was burned off the catalyst at 510°C prior to reduction.

Unfortunately, the presence of halogens such as chlorine or fluorine or their compounds during regeneration results in the formation of corrosive by-products such as HCl and NH₄Cl. These compounds can cause damage to equipment used in the reforming process such as heat exchangers, liquid/gas separators and reactor internals. The halogen containing compounds and their products necessary for platinum

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redispersion are highly toxic as well. Therefore, it is highly desirable to have available a catalyst regeneration procedure that does not include the use of a halogen containing gas.

U.S. Patent No. 5,073,529, issued December 17, 1991 to Miller et al., describes a process for regenerating a coke-deactivated reforming catalyst. A two-step carbon burn procedure is used wherein the catalyst is initially contacted with oxygen and an inert gas at a temperature ranging from 500-700°F. During the second step, the catalyst is contacted with oxygen and an inert gas at a temperature ranging from 850-950°F.

SUMMARY OF THE INVENTION

The present invention relates to a halogen-free process to regenerate a coke contaminated catalyst comprising platinum on a molecular sieve support which process comprises contacting said catalyst with an oxygen-containing gas at a temperature of from 300°F to no more than about 780°F. More particularly, it relates to a process to regenerate a coke contaminated catalyst comprising contacting said catalyst with a halogen-free oxygen-containing gas at a maximum temperature of less than 780°F for a sufficient period of time such that the aromatization activity is restored to within 20°F of the aromatization activity the catalyst possessed at the start of the previous run cycle. By the term "aromatization activity" we mean the extrapolated start-of-run temperature where the run conditions and the feed as well as the aromatics yield are substantially the same as in the previous run cycle. By the practice of the present invention, the platinum on the catalyst remains sufficiently dispersed on the support to allow for an

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activity change of not more than 20°F upon termination of the regeneration procedure, and return of the catalyst to hydrocarbon conversion service. Thus, the catalyst aromatization activity is based upon the temperature needed to achieve a desired constant aromatics production. Typically, we have controlled our process to about 40 to 42 wt.% aromatics in the product, although other values may be set, in other circumstances. Regeneration by the process of the present invention results in a catalyst which has an aromatization activity, as defined above, which is within 20°F of the temperature needed in the previous run to achieve the same constant aromatics production.

Among other factors, we have found that by limiting the ultimate temperature in the carbon burn regeneration procedure to a maximum temperature of less than 780°F, preferably between 600°F to 750°F the catalyst may be restored to an activity very close to that of the fresh catalyst, without requiring a metal re-dispersion step. It is further preferred the carbon burn be initiated at a temperature of less than about 500°F and further that the recycle gas be dried to achieve a water concentration in the recycle gas of less than 1000 ppm water, prior to the recycle gas entering the reforming reactor train.

We have found that by avoiding addition of a halogen or halogen containing gas during or after the carbon burn procedure, plant deterioration due to stress cracking and corrosion is minimized. Further, prior to our present invention, it was common practice to circulate soda ash or morpholine solutions through effluent heat exchangers, transfer lines, and liquid-gas separators during the regeneration of reforming catalyst in order to prevent corrosion due to chlorides. The need to use corrosion

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inhibitor solutions is eliminated when regenerating reforming catalyst by the method of the present invention.

In general, the art teaches away, i.e., describes high temperature burn procedure followed by redispersion step or, burn/redispersion combined. We have now, surprisingly, found that if the coke burn and reduction are both done at low temperatures and with low concentration of water, the regenerated catalyst has excellent activity and unexpectedly long life.

Surprisingly, we have also found that the rate of deactivation or "fouling rate" of the regenerated catalyst decreases following the application of the regeneration process of the present invention. Thus, a catalyst regeneration procedure was discovered in which noble metal does not appreciably agglomerate; eliminating the need for a redispersion step, which are among the advantages of using the present regeneration method on a Pt containing molecular sieve type catalyst.

DETAILED DESCRIPTION OF THE INVENTION

As explained in the summary section above, the present invention is a procedure for regenerating reforming catalysts, comprising platinum on a molecular sieve support.

By the term "reforming" we mean the process of converting paraffins, naphthenes or olefins to aromatic hydrocarbons via hydrodecyclization or dehydrogenation. Feeds useful in reforming typically include hydrocarbons having from six to eleven carbon atoms, but these feeds can also include narrower cuts, such as a C₆ to C₇ cut. Indeed, the reforming catalysts that can be regenerated by the process of this

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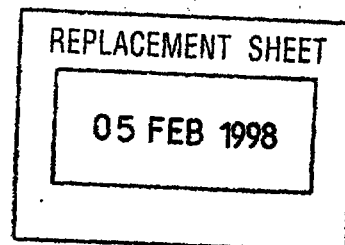
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invention can be used to make chemicals as well as gasoline components. For example, benzene, toluene or mixtures thereof can be produced by reforming hydrocarbons having six to seven carbon atoms.

The catalysts advantageously regenerated by the method of this invention comprise platinum on a molecular sieve support. Molecular sieves are defined as porous materials which exhibit the property of acting as sieves on a molecular scale. The molecular sieves of most interest for catalysis are those which have uniform pore sizes in the 4.2 to 15 Angstrom diameter range, particularly crystalline materials of the aluminophosphate, aluminosilicate, and pure silica types. The aluminosilicate molecular sieves include zeolites and certain modified clays.

Examples of aluminophosphate molecular sieves include ALPO-5, ALPO-11, ALPO-31, ALPO-34, and ALPO-41, as well as isostructural materials containing silicon, cobalt, manganese, magnesium, iron, chromium, titanium, or other elements as part of the crystalline framework. Zeolite molecular sieves of particular interest include zeolite types X, Y, and L, mordenite, ZSM-5, ZSM-12, ZSM-20, SSZ-25, SSZ-26, and beta zeolite. Examples of modified clays with molecular sieving properties include pillared bentonites and hectorites. Silicalite and SSZ-24 are examples of molecular sieves composed of substantially silica. Silicalite has the same crystal structure as ZSM-5 except that substantially all of the aluminum atoms have been replaced with silicon atoms. SSZ-24 is the all-silica structural analog of ALPO-5.

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Catalyst Description

In copending Application Serial No. 496,119, assigned to the assignee of the present invention and entirely incorporated by reference herein, an intermediate pore size crystalline silicate having a silica to alumina ratio of preferably at least 500, is described. We have found the present catalyst regeneration process may be advantageously used to regenerate the intermediate pore size crystalline silicate catalyst, and that the present process may also be advantageously applied to a mixed catalyst system comprising the intermediate pore size crystalline silicate described in copending Application Serial No. 496,119.

A preferred catalyst to regenerate by the process of this invention comprises platinum on an alkaline earth or alkali metal exchanged, L-zeolite. It is especially preferred that this catalyst be protected from sulfur poisoning during its use in reforming, so that the catalyst is never contacted with more than 100 ppb by weight sulfur in the feed. This can be accomplished by using a sulfur converter/sorber system as described in U.S. Patent No. 4,925,549 to Robinson et al. The regeneration process of this invention is especially effective on substantially sulfur free catalyst.

In addition to platinum, the catalysts regenerated by the present invention may contain elements such as rhenium, tin, germanium, iridium, copper, iron, cobalt, nickel, and titanium which in certain cases may improve catalyst selectivity or stability. For naphtha reforming, it is desirable that the molecular sieve catalyst have a low acidity. Acid sites may be neutralized by ion exchange with alkali ions such as lithium, sodium, potassium, cesium and rubidium ions or alkaline earth ions such as calcium,

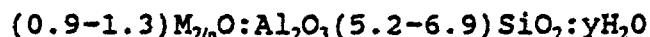


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magnesium, strontium, and barium. With zeolites, low acidity may also be achieved by substituting boron for aluminum in the zeolite framework; for example, boron substituted beta zeolites or by using a zeolite with a silica/alumina ratio greater than 500.

The present invention has been found to be particularly effective when applied to large-pore zeolites. Large-pore zeolites are defined as zeolites having an effective pore diameter of between 6 and 15 Angstroms. Among the large-pore zeolites which have been found to be useful as reforming catalysts, L-type zeolites are the most important. Other important zeolites include X-zeolites, Y-zeolites, mordenites, and zeolite beta.

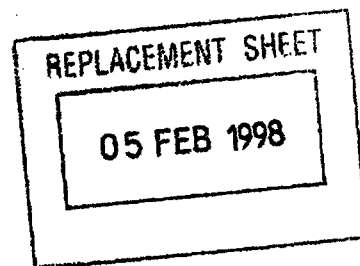
A typical composition of L-type zeolites, expressed in terms of mole ratios of oxides, may be represented as follows:



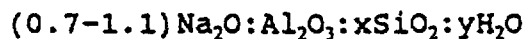
wherein M designates a cation, n represents the valance of M, and y may be any value from 0 to 9. Zeolite L, its X-ray diffraction pattern, its properties and method for its preparation are described in detail in U.S. Patent No. 3,216,789 which is hereby incorporated by reference. The true formula may vary without changing the crystalline structure. For example, the mole ratio of silicon to aluminum (Si/Al) may vary from over a range which is typically 1.5 to 3.5, but may be higher. The barium exchanged form of zeolite L is particularly preferred as described, for example, in U.S. Patent Nos. 4,434,311 and 4,547,472.

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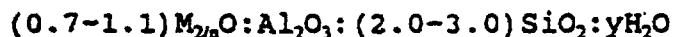
The chemical formula for zeolite Y expressed in terms of oxide molar ratio may be written as:



wherein x is a value between 3 and 6, and y may be a value up to 9. Zeolite Y has a characteristic X-ray diffraction pattern which may be employed with the above formula for identification. Zeolite Y is described in more detail in U.S. Patent No. 3,130,007. U.S. Patent No. 3,130,007 is hereby incorporated by reference herein to show a zeolite useful in the present invention.

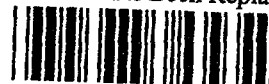
More recent patents disclose high silica/alumina versions of zeolite Y produced by steaming and/or chemical extraction which removes aluminum from the framework of the originally synthesized zeolite. Y-zeolites with framework silica/alumina ratios as high as 50:1 or higher may be prepared by these methods, and are useful supports for the reforming catalysts regenerated by the method of the present invention.

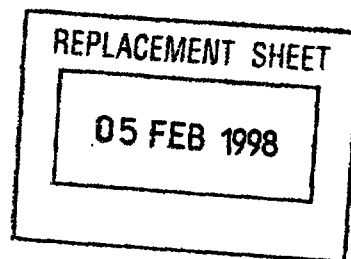
Zeolite X is a synthetic crystalline zeolitic molecular sieve which may be represented by the formula:



wherein M represents a metal, particularly alkali and alkaline earth metals, n is the valence of M, and y may have any value up to about 8 depending upon the identity of M and the degree of hydration of the crystalline zeolite. Zeolite X, its x-ray diffraction pattern, its properties and method for its preparation are described in detail in U.S. Patent No. 2,882,244, which is hereby incorporated by

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reference in its entirety to show a zeolite useful in the present invention.

Zeolite beta is a known synthetic crystalline aluminosilicate originally described in U.S. Patent Nos. 3,308,069 and RE 28,341 to which reference is made for further details of this zeolite, its preparation and properties. These references describe the composition of zeolite beta in its as-synthesized form as follows:



where X is less than 1, preferably less than 0.75, TEA represents tetraethylammonium ion, Y is greater than 5 and less than 100, and W is up to about 4, depending on the condition of dehydration and on the metal cation present. These references also teach that the sodium ion may be replaced by another metal ion using ion exchange techniques. Subsequent publications such as European Patent Applications Nos. 95,304; 159,846; 159,847; and 164,939 have broadened the definition of zeolite beta to include materials prepared using templating agents other than tetraethylammonium hydroxide and materials having a Si/Al ratio greater than 100. Also the zeolite described in European Patent Application No. 55,046 ("Nu-2") and British Patent Application No. 2,024,790 ("Borolite B") have structures and X-ray diffraction patterns similar to that of zeolite beta and are included within the scope of the term "zeolite beta" as used herein.

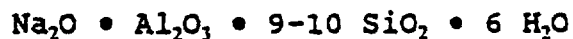
Mordenite is a commercially available zeolite which occurs in nature and has also been synthesized. Both "small port" and "large port" mordenites have been synthesized. The "large port" form is preferred for catalysis and is

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described in "Zeolite Molecular Sieves" by Donald W. Breck, published by John Wiley and Sons. A typical oxide composition is:



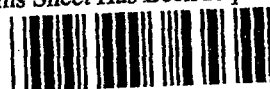
The silica/alumina ratio may be increased by extracting alumina using various chemical and thermal methods similar to those employed with zeolite Y.

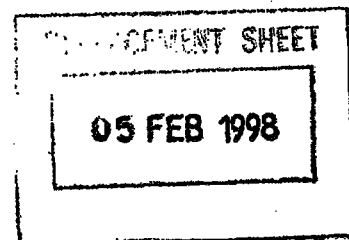
The percentage of platinum in the catalyst is between 0.1% and 10%, the lower limit corresponding to minimum practical catalyst activity and the upper limit to roughly the maximum possible platinum utilization. Preferably, the catalyst contains between 0.2 and 5.0 percent platinum. Group VIII metals are introduced into a large-pore zeolite during synthesis, impregnation or ion exchange in an aqueous solution of an appropriate metal salt. If it is desired to introduce two Group VIII metals onto the large-pore zeolite, the operation may be carried out simultaneously or sequentially.

By way of example, platinum can be introduced by impregnating the large-pore zeolite with an aqueous solution of tetrammineplatinum (II) nitrate $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, tetrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, or diammineplatinum $[\text{Pt}(\text{NH}_3)_2](\text{NO}_2)_2$. In an ionic exchange process, platinum can be introduced by using cationic platinum complexes such as tetrammineplatinum (II) nitrate.

A binder may be used in the preparation of the catalysts. An inorganic oxide is used as a matrix to bind the large-pore zeolite. This binder can be a natural or a synthetically produced inorganic oxide or combination of

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inorganic oxides. Typical inorganic oxide binders which can be used include clays, alumina, silica or mixtures thereof. Preferable binders are alumina, silica, or mixtures thereof. Acidic sites on the binder are preferably exchanged by cations which do not impart strong acidity (such as sodium, potassium, rubidium, cesium, calcium, strontium or barium).

After the desired metal or metals have been introduced, the catalyst is typically calcined in air and then reduced in a hydrogen environment.

The regeneration process of the present invention may be useful on catalysts in the physical form of extrusions, spheres, pills, pellets, granules, broken fragments, or various other shapes known in the art.

Catalyst Use and Contamination

The reforming catalysts regenerated by the process of the present invention are used for aromatization of C_6 to C_{11} , preferably C_6 and C_7 non-aromatic hydrocarbons. Accordingly, a hydrocarbon feedstream which comprises a C_6 to C_{11} paraffin, olefin, or naphthene, is contacted with the catalyst at aromatization conditions. Aromatization conditions typically include an absolute pressure of from about 0.5 to about 50.0 atmospheres, with the preferred pressure being from about 1.0 to about 10.0 atmospheres, a temperature of from about 800°F to about 1200°F, preferably 800°F to 1050°F, and a liquid hourly space velocity of from between about 0.1 to about 10 per hour. Preferably, hydrogen is employed in the process. When present, hydrogen may be circulated at a rate of from about 1.0 to about 10.0 moles of hydrogen per mole of hydrocarbon in the hydrocarbon feedstream. Feed streams entering the reforming reactors

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should be low enough in sulfur and water to prevent catalyst deactivation by sulfur poisoning or platinum sintering.

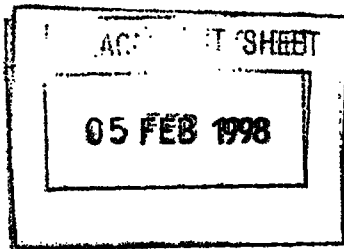
Catalyst Regeneration Method

The gradual accumulation of coke and other deactivating carbonaceous deposits on the catalyst will eventually reduce the activity of the catalyst and selectivity of the aromatization process. Typically, catalyst regeneration becomes desirable when from about 0.5 to about 3.0 wt. % or more of carbonaceous deposits are laid down upon the catalyst. At this point, it is typically necessary to take the hydrocarbon feedstream out of contact with the catalyst and purge the hydrocarbon conversion zone with a suitable gas stream. The catalyst regeneration method of the present invention is then performed either by unloading the catalyst from the conversion zone and regenerating in a separate vessel or facility or performing regeneration in-situ. Alternatively, the catalyst may be continuously withdrawn from the reactor for regeneration in a separate vessel, to be returned to the reactor as in a Continuous Catalytic Reformer.

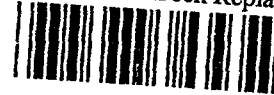
In fixed bed operation, it may sometimes be necessary to dump the catalyst from the reactors and screen out fines in order to reduce pressure drop. This typically occurs after several years of operation. The dump and screen procedure is usually done in combination with a catalyst regeneration. First carbon is burned off the catalyst following the procedures of this invention. This also serves to reoxidize finely divided metals on the catalyst such as iron and platinum. In their metallic form, these metals will rapidly oxidize when exposed to air and possibly ignite a fire or explosion when hydrocarbons are also present.

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The catalyst is then dumped from the reactors into a screening device where the fines are removed. It is then reloaded into the reactors and dried by circulating nitrogen through the reactors and recycle gas dryer while heating to reduction temperature. When water levels in the reactor effluent are sufficiently low, the catalyst is then reduced according to the procedures of this invention and returned to reforming service. The dryout time can be shortened and the catalyst protected from water, carbon dioxide, and sulfur compounds in the atmosphere by blanketing with nitrogen or dry air during the dumping, screening, and reloading processes.

According to the catalyst regeneration method of the present invention, the essential step of the method incorporates a lower temperature carbon burn step. The lower temperature carbon burn step involves contacting the deactivated catalyst with a gaseous mixture of oxygen and an inert gas. The oxygen is typically derived from air and an inert gas serves as a diluent, such that oxygen concentration is from about 21 mole % oxygen to a lower limit which for the practice of the present invention may be as low as 0.1 mole % oxygen. The practice of the present invention is not limited to use of air, however, and higher levels of oxygen may be used in methods where oxygen is supplied in a more pure form such as from cylinders or other containing means. Typical inert gases useful in the low temperature carbon burn step may include nitrogen, helium, carbon dioxide, and like gases or any mixture thereof; nitrogen being preferred. The regeneration gases should be substantially sulfur-free as they enter the reactor, and preferably contain less than 100 part per million by volume water. Because the oxygen content determines the rate of burn, it is desirable to keep the oxygen content low so as

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not to damage the catalyst by overheating and causing metal agglomeration, while still conducting the carbon burn step in a manner that is both quick and effective. We have found it desirable to keep the oxygen level in the inlet to the regeneration vessel between 0.2 to 4.0 mole % during the practice of the present invention to avoid thermal damage to the catalyst, and still allow for the regeneration process to be accomplished in a reasonable amount of time.

The low temperature carbon burn process of the present regeneration method occurs at a temperature of between 300°F to 780°F. Other conditions present during the low temperature carbon burn step include a pressure sufficient to maintain the flow of the gaseous oxygen containing mixture through the catalyst zone such as a pressure of between about 1.0 to 50.0 atmospheres and preferably from about 2 to about 15 atmospheres, and a gas hourly space velocity of about 100 to about 10,000 per hour, with a preferred value of about 500 to about 5,000 per hour.

The regeneration method of the present invention is performed in a halogen-free environment. By halogen-free, we mean that chlorine, fluorine, bromine, or iodine or their compounds including for example, hydrogen chloride, carbon tetrachloride, ethylene dichloride, propylene dichloride; are not added at anytime during the catalyst regeneration process.

It is desirable to keep water levels low during the reforming reactions and during the regeneration procedure. This is especially true when temperatures are above 700°F. Although short periods of time (several minutes) at water levels as high as saturation can be tolerated at 700°F and higher, it is desirable to avoid this high a water level.

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A preferred embodiment of the present invention includes the use of a dryer in combination with flowing at least a portion of the combustion gas resulting from the contacting of the catalyst with the oxygen containing gas to a dryer and recycling the dried combustion gas to the catalyst zone. We have found that drying the recycle gas further reduces catalytic metal agglomeration, resulting in a more active regenerated catalyst. It is preferred that water in the recycle gas be reduced to less than 1000 ppmv, more preferably less than 10 ppmv, prior to the gas being recirculated to the catalyst zone. We have found results to be best when a fresh dryer is employed just prior to the beginning of and throughout the coke-burn step.

In the preferred embodiment of the present invention, the low temperature carbon burn step results in removing most of the carbonaceous material from the catalyst while leaving an amount of from between 0.1 to about 0.5 wt. % carbon on the catalyst. Although the present invention is not limited by any theory of operation, one possible explanation of the resulting improved catalyst performance is that the small amount of carbon remaining on the catalysts locates at the acid sites, and thus significantly decreases the fouling rate of the regenerated catalyst. Surprisingly, we have also found the yield of C_3+ product to increase slightly after a first regeneration of the catalyst.

Further, in another preferred embodiment of the present invention, the first reactor inlet temperature is increased during the carbon burn in a step-wise fashion over a period of about one to five days from an initial temperature of less than 500°F, preferably between 300°F and 500°F to achieve a final peak catalyst bed temperature of less than 780°F, preferably between about 600°F and 750°F.

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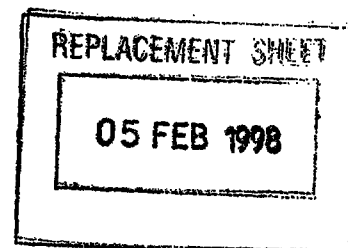
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The oxygen concentration at the first reactor inlet should be controlled in the process of the present invention so as to limit exotherms and high moisture levels due to hydrocarbon combustion. Therefore, in the practice of a preferred embodiment of the present invention, the oxygen is maintained at a level between about 0.2 mole % and 2.0 mole % in the oxygen containing gas throughout the carbon burn-off step. During the initial stages of the burn, it is preferred the oxygen level be maintained at a level between 0.2 and 0.5 mole %. As the rate of burn subsides, oxygen levels may be increased to between 0.5 and 4.0 mole %.

The resulting regenerated catalyst with a portion of carbonaceous material burned off is thereafter typically cooled to about 500°F and purged with nitrogen or another inert gas to displace the oxygen and any water therefrom. The exit gas is easily monitored to determine when the catalyst zone is substantially free of oxygen and water.

After the low temperature carbon burn-off and purge, the catalyst is activated by treatment with hydrogen. In the initial reduction step, the catalyst is contacted with a hydrogen containing stream at a temperature of from about 300°F to about 700°F for a period of at least of about 0.1 to about 10.0 hours. Preferred conditions for the reduction step are from about 400°F to about 600°F for a period from about 0.1 to about 2.0 hours. The pressure and gas rates utilized in the reduction step are preferably very similar to those above described in the low temperature carbon burn step. Following the initial reduction, the catalyst may be further reduced and dried by circulating a mixture of inert gas and hydrogen while raising the temperature to between 900 and 1000°F. In the reduction step, metallic components





are returned to their elemental state and the resulting regenerated catalyst possesses activity, and selectivity characteristics quite similar to those occurring in a fresh catalyst. Additionally, we have found the regenerated catalyst has improved stability, as measured by a decreased fouling rate. When iron oxides are present on the catalyst or in the piping, it is desirable to use at least a 4:1 mole ratio of nitrogen to hydrogen during the reduction and dryout procedure, in order to limit the formation of NH_3 to less than 200 ppmv.

After completing the reduction step, the temperature is lowered to 800°F or less. The reforming process in which the catalyst is employed may be resumed by charging the hydrocarbon feedstream to the catalyst zone and adjusting the reaction conditions to achieve the desired conversion and product yields.

The following examples are intended to further exemplify the invention, and are not intended to limit the invention in any way.

LOW TEMPERATURE REGENERATION

EXAMPLE I

Pretreatment and Composition of Naphtha Feedstock

A hydrocarbon feedstock was hydrotreated and dried to remove sulfur, oxygen, and water. The treated feed was stored under nitrogen to keep it substantially free of water and oxygen. The sulfur content of the hydrotreated feed was about 0.1 ppmw. A gas chromatographic analysis showed the following composition.

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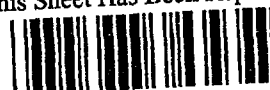
	<u>LV%</u>
i-pentane	0.0
n-pentane	0.5
2,2-dimethylbutane	2.2
2,3-dimethylbutane	3.5
2-methylpentane	17.9
3-methylpentane	14.5
n-hexane	20.0
2,2-dimethylpentane	1.3
2,4-dimethylpentane	1.7
2,3-dimethylpentane	2.8
2-methylhexane	7.5
3-methylhexane	8.5
n-heptane	4.5
C ₈ + paraffins	2.1
cyclopentane	1.2
methylcyclopentane	4.9
cyclohexane	2.0
methylcyclohexane	0.5
other C ₆ - C ₇ naphthenes	1.7
benzene	0.2
toluene	0.7
ethylbenzene	0.2
heavies	1.6

EXAMPLE II

First Run Cycle Starting with Fresh Catalyst

Eighty cubic centimeters of fresh reforming catalyst were charged to a one-inch diameter tubular reactor. The catalyst comprised platinum on barium exchanged L-zeolite and a binder. The reactor was installed in a naphtha reforming pilot plant inside a three-zone electric furnace. Catalyst bed temperatures were measured by six equally spaced thermocouple points located from the top to the bottom of the catalyst bed in an axial thermowell. The

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pilot plant was purged and pressure tested with nitrogen, depressured, then pressured to 100 psig with a blend of 1.0% oxygen in nitrogen and the recycle compressor started. The reactor effluent passed through a chilled liquid-gas separator, a moisture analyzer, a dryer containing 4 Å molecular sieves, a compressor, a mass flowmeter, and back to the reactor. The gas circulation rate was adjusted to 0.7 standard liters per minute. A small amount of the recycle gas was allowed to bleed off the recycle loop and makeup oxygen/nitrogen blend was fed from a cylinder.

The catalyst was dried by circulating the oxygen/nitrogen blend and heating the to 500°F. The temperature was held at 500°F until the reactor effluent contained less than 300 ppm water. The furnace temperature was then raised to 600°F and held until water in the reactor effluent again was less than 300 ppm. Finally, the temperature was raised to 700°F and held until the reactor effluent contained less than 100 ppm water. The reactor was cooled to 500°F and the oxygen/nitrogen makeup gas replaced with dry nitrogen. The pilot plant was purged of oxygen and the pressure adjusted to 70 psig with the compressor continuing to operate at the same setting.

Catalyst reduction was initiated by switching the makeup gas from nitrogen to hydrogen and pressuring from 70 psig up to 100 psig. The compressor setting was then readjusted to again obtain a circulation rate of 0.7 standard liters per minute. After holding at 500°F for an hour, the reactor furnace reactor temperature was raised to 700°F at rate of 50°F/h. The temperature was held at 700°F until water in the reactor effluent was less than 300 ppmv and then raised to 800°F at 50°F/h. When moisture in the reactor effluent again fell below 300 ppmv, the temperature was raised to



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900°F and held until water in the reactor effluent was less than 100 ppmv. The furnace temperature was then lowered to 800°F and preparations were made for naphtha feed introduction. This included putting a sulfur converter/sorber reactor on-line in the recycle loop between the naphtha feed introduction point and the reforming reactor. The purpose of the sulfur converter/sorber was to reduce sulfur compounds in the feed entering the reforming reactor to below 5 ppbv.

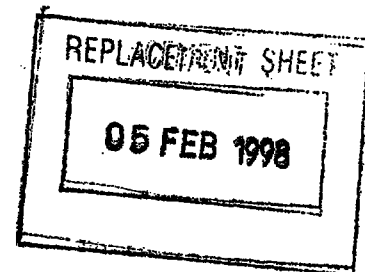
The naphtha feed from Example I was fed at a rate of 128 mL/h corresponding to a liquid hourly space velocity (LHSV) of 1.6 volumes of feed per volume of catalyst per hour. Pressure was controlled at 100 psig by allowing product hydrogen gas to exit the recycle loop through a back pressure regulator. The product hydrogen stream was analyzed and the hydrogen recycle rate was adjusted to obtain a hydrogen to naphtha feed molar ratio of 3.0. Liquid product was collected in the separator at 60°F. A level control and valve allowed the separator to drain into a debutanizer still which produced a C₃ liquid product.

After feed introduction, the furnace temperature was rapidly raised until the catalyst aromatization activity was able to produce a liquid product comprising 42 wt. % aromatics. The yield of liquid product was about 85 LV% on feed. Thereafter as the catalyst deactivated temperatures were raised to maintain constant aromatics in the liquid product.

In order to determine aromatization activity in terms of a start-of-run temperature, the following procedure was used. After an initial lineout period, the average catalyst bed temperature was plotted against time to determine the catalyst deactivation rate. Such plots are generally linear

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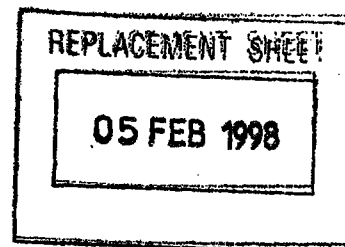
and may be fitted by the least squares method. The slope of the line is the catalyst deactivation rate and the start-of-run temperature is defined as the zero time intercept. An approximate eventual run length is estimated by making a linear extrapolation to the end of run temperature. At end of run, aromatics selectivity begins to decrease and catalyst deactivation accelerates markedly. The end of run temperature was expected to be 935°F for the feed and run conditions above.

After startup, the pilot plant ran at constant LHSV, recycle ratio, pressure, and aromatics for 658 hours. A least squares fit of the reaction temperature data yielded a fouling rate of 0.026°F/h and a start-of-run temperature of 855°F. Assuming an end of run temperature of 935°F, the eventual run length would have been about 3100 hours if the reaction conditions had remained unchanged.

After 658 hours on-stream, reaction conditions were changed in order to study process variable effects. The run continued under various conditions for a total of 3810 hours. At the end of the run, the naphtha feed was stopped and hydrogen circulation was continued while the reactor furnace cooled to 500°F. The unit was then purged with nitrogen and allowed to cool to ambient temperature. Finally, the reactor was blocked off under nitrogen pressure and the catalyst saved for a future regeneration.

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Catalyst reduction was initiated at 500°F by depressuring to 70 psig and then pressuring up to 100 psig with hydrogen while the compressor continued to operate. The makeup gas was switched from nitrogen to hydrogen. The temperature was held at 500°F for one-hour and then raised 4°F/h to 900°F. The temperature was held at 900°F for 16 hours before cooling to 800°F for naphtha feed introduction.

EXAMPLE IV

Catalyst Performance After First Regeneration

After catalyst regeneration, the naphtha reforming reaction was resumed with the same conditions and feed used in Example II. Liquid product yields were the same as before regeneration and slightly better than with fresh catalyst. After 840 h on stream a least squares fit was made as before to determine the start-of-run temperature and deactivation rate. The start-of-run temperature was 859°F and the catalyst deactivation rate was 0.017°F/h. Thus, the catalyst activity had been restored to within 4°F of fresh catalyst. Surprisingly, the catalyst deactivation rate was significantly less than with fresh catalyst. The projected run length was 4300 hours compared to 3100 hours for the first cycle.

After determining start-of-run temperature and catalyst deactivation rate, the liquid hourly space was increased to 3.0 and the furnace temperature was increased to obtain a maximum catalyst bed temperature of 1025°F in order to accelerate catalyst fouling. After 1464 hours at these conditions, the catalyst had reached approximately end of run activity and the liquid hourly space velocity was reduced to the original value of 1.6. The average catalyst



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bed temperature to produce a liquid product containing 42 wt. % aromatics was then determined to be 939°F. The catalyst had aged 80°F from the start of the second run cycle.

EXAMPLE V

Second Regeneration of the Catalyst

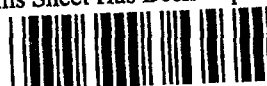
At the conclusion of the run cycle described in Example IV, the naphtha feed was stopped and the reforming reactor was cooled to 500°F while continuing to circulate hydrogen. At 500°F, the recycle loop was purged with nitrogen, the sulfur converter/sorber was taken off-line, and the separator was drained. Purging continued while the reactor cooled to 300°F.

The catalyst was then regenerated following substantially the same procedure used in Example III.

EXAMPLE VI

Catalyst Performance Following Second Catalyst Regeneration

After the second regeneration, the reforming reaction was restarted with same conditions and feed used at the start of the first and second run cycles. After 660 hours, a least squares fit was again made to determine the start-of-run temperature and catalyst deactivation rate. The start-of-run temperature was determined to be 874°F and the catalyst deactivation rate was 0.012°F/h. The projected run length at these conditions was therefore about 5000 hours. The start-of-run temperature had declined 13°F from the start of previous run cycle, but the catalyst deactivation



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rate was again reduced so that projected run length had increased. The liquid C_3^+ yield was the same as after the first regeneration.

EXAMPLE VII

Regeneration without Dryer

A coked catalyst from a 4700 hour pilot plant run was saved and later returned to service at the same conditions used in the previous examples. Prior to its use, the catalyst had the same composition as the catalyst used in Example II. After 330 hours on-stream, the average catalyst bed temperature was 930°F and liquid product contained 42 wt. % aromatics. The yield of liquid product on feed was beginning to decline and was 85.5 LV%.

At this point the naphtha feed was stopped and the reactor cooled to 500°F in circulating hydrogen. At 500°F, the recycle loop was purged with nitrogen and the sulfur converter/sorber reactor and recycle gas dryer were bypassed and the separator was drained. The pressure was adjusted to 85 psig. This time the carbon burn was started at 500°F. Air and oxygen/nitrogen blend were added to the recycle gas stream as in Examples III and V, but the oxygen content at the reactor inlet was adjusted to 0.5% instead of 1.0%. The dryer remained bypassed throughout the burn. There was complete oxygen conversion and the exotherm was about 12°F. After holding at 500°F for 1.5 hours, the furnace temperature was raised 25°F/h to 700°F. Oxygen breakthrough occurred when the furnace temperature reached about 640°F. There was only a small amount of burning by the time the furnace temperature reached 700°F and the exotherm was negligible. Reactor inlet oxygen level was raised to 1.0%

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and the temperature held at 700°F for 20 hours to complete the burn. The exotherm during the final burn was less than 2°F.

Since the recycle gas dryer was bypassed, water built up in the recycle gas during the burn until it reached saturation levels in the separator. Moisture levels in the recycle gas exceeded 2000 ppm well into the 700°F hold period.

After completing the carbon burn, the recycle loop was purged with nitrogen and the reactor was cooled to 500°F while recycle gas circulation continued. At 500°F the dryer and the sulfur converter/sorber were put back on line. When water in the recycle gas fell below 100 ppmv, the plant was pressured up 100 psig with hydrogen to initiate catalyst reduction. After an hour at 500°F, the reactor was heated to 900°F at rate of 10°F/h. The reactor was held at 900°F until the moisture content of the reactor effluent was less than 100 ppm then cooled to 800°F for feed introduction.

EXAMPLE VIII

Catalyst Performance after Regenerating without a Dryer

After the catalyst regeneration in Example VII, the naphtha feed was restarted and the reforming reaction resumed for 590 hours. The feed and the run conditions were the same as in Example II. Catalyst performance was not as good as obtained in Examples II, IV, or VI. The start-of-run temperature was 868°F and the fouling rate was 0.031°F/h. The projected run length was therefore only about 2100 hours.

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EXAMPLE IX

Regeneration with Dryer

The regeneration procedure of Example VIII was repeated with another coked catalyst sample except that the recycle gas dryer was employed during the carbon burn and consequently the reactor inlet moisture levels were always less than 5 ppm. The catalyst composition prior to its use as a reforming catalyst was the same as that used in Examples II and VII.

EXAMPLE X

Catalyst Performance After Regeneration with Dryer

The catalyst regenerated in Example IX was tested with the same run conditions and feed as in Example VIII. After 576 hours on-stream, the start-of-run temperature was 862°F and catalyst deactivation rate was 0.019°F/hr. The projected run length was 3800 hours compared to 2100 in Example VIII.

The results of from Examples I to X are summarized in Table 1 below.

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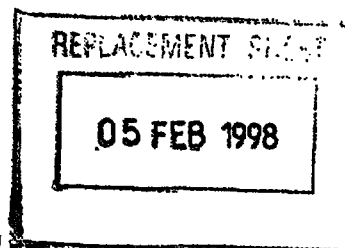
TABLE 1

<u>Description</u>	<u>Examples</u>	<u>Start of Run Temp. °F</u>	<u>Deactivation Rate °F/h</u>	<u>Projected Run (hours)</u>
Fresh Catalyst	II	855	0.026	3100
First Regeneration	II-IV	859	0.017	4100
Second Regeneration	V-VI	874	0.012	5000
Regeneration without Dryer	VII-VIII	868	0.031	2100
Regeneration with Dryer	IX-X	862	0.019	3800

The Table clearly shows that a controlled low temperature carbon-burn regeneration procedure restores most of the activity present at the start of the previous run cycle and that catalyst deactivation rates are significantly reduced, such that several cycles are possible before there is a need for platinum redispersion. The results further show the advantage in using a dryer to reduce the water content of the recycle gas during the carbon burn. These results are surprising in view of the prior art and afford the opportunity to increase cycle length and avoid the use of corrosive and sometimes highly toxic halogen compounds during regeneration.

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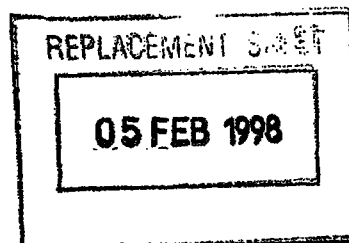
EXAMPLE XI

Regeneration Procedure for a Large-Scale Plant

Allowing for differences in the exotherm as compared to a pilot plant, a commercial unit with four reactors in series is regenerated as follows. Naptha feed is withdrawn and hydrogen is circulated at high temperature to strip hydrocarbon from the catalyst. The separator and knockout drums are periodically drained of hydrocarbon. Hydrogen circulation is continued while the reactors are cooled to about 420°F. At 420°F, the recycle loop is purged with nitrogen and low points are checked for liquid hydrocarbons. After periodic draining shows that little or no hydrocarbon liquids are being collected, it is advantageous to switch to a fresh recycle gas dryer which is substantially free of hydrocarbons and water. If there is a recycle gas sulfur converter/sorber, it will be bypassed at this point.

When the reactor inlets are at 420°F and the level of combustibles in the recycle gas is less than 2.0%, air is introduced to the recycle gas stream. The oxygen level at the first reactor inlet is adjusted to 0.5%. The burning of residual combustibles in the recycle gas consumes all the oxygen and results in an 80 to 125°F exotherm across the first reactor. Eventually, the vapor-phase combustibles are consumed and the burn-wave moves through the reactor chain. After oxygen breakthrough occurs and the exotherm subsides, furnace temperatures are raised at rate of about 25°F/h until peak catalyst bed temperature reaches 700°F. The total exotherm at this point is less than about 20°F. When oxygen conversion across the reactor train drops to less than 10%, the oxygen concentration at the reactor inlet is raised to 1.0 to 4.0% and the furnace temperatures are





adjusted to maintain the peak catalyst bed temperatures as close to 700°F as possible.

Temperatures are maintained at 700°F for 12 to 24 hours before the air makeup is stopped. The recycle loop is then purged with nitrogen and cooled to 500°F. At 500°F the recycle gas dryers are switched again and the sulfur converter/sorber is brought back on-line. About twice the stoichiometric amount of hydrogen needed for reduction of the catalyst is fed into the unit over a period of about an hour. The unit is then partially depressured and pressured up with hydrogen to adjust the hydrogen to nitrogen ratio to about one-to-four. Higher hydrogen to nitrogen ratios can result in excessive ammonia formation, which is catalyzed by the iron particles present in the reactor tubes. The temperature is held at 500°F for about an hour then raised 10°F/h to 900°F. The hydrogen/nitrogen ratio is maintained by adjusting hydrogen and nitrogen makeup rates. The temperature is held at 900°F for at least 12 hours. When water in the fourth reactor effluent is less than 100 ppm, the temperature is dropped to 700°F or lower to await feed introduction.

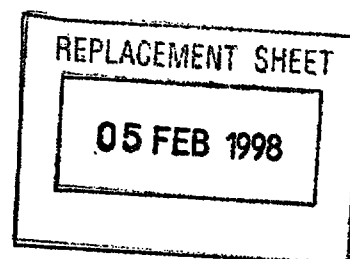
EXAMPLE XII

Reforming With A Silicalite Catalyst/Catalyst Coking

A silicalite catalyst was produced by impregnating a dried, synthesized Silicalite powder to give 1% Pt on the Silicalite powder, then mixing this with SAPO-11 powder to produce a finished catalyst consisting of 25% wt SAPO-11 and 75% wt Pt Silicalite.

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This catalyst was used to convert hexane containing feeds to aromatics. The feed compositions are listed in Table 3. The conversion conditions used were a pressure of 30 psig, a WHSV of 0.72, a hydrogen to hydrocarbon ratio of seven to one, with the catalyst temperatures ranging from 880 to 1000°F to maintain a high product benzene level and adjust for fouling.

EXAMPLE XIII

Regeneration Of Silicalite Catalyst

The catalyst of Example XII was repeatedly coked and regenerated. The regeneration conditions included treating the catalyst with low concentrations (0.5 to 2.0 wt. %) of oxygen at 30 to 100 psig at a GHSV of 923. During regeneration, the regeneration gases contained less than 100 ppm water.

The regeneration temperature was varied over the range of 450 to 680°F. Regenerations below about 500°F for 16 to 24 hours were not successful in producing a catalyst having an activity (as measured by hexane conversion) or a selectivity (as measured by the wt. % benzene in the product) similar to fresh catalyst. At regeneration temperatures between 550 and 680°F, aromatization activity was restored to about that of the start of the run cycle.

Table 2, below, shows the regeneration temperatures and times for several of these regenerations, along with the activity and selectivity results. The regenerated catalyst was able to maintain product benzene levels of about 40 wt. %, for greater than 1000 hours between regenerations.



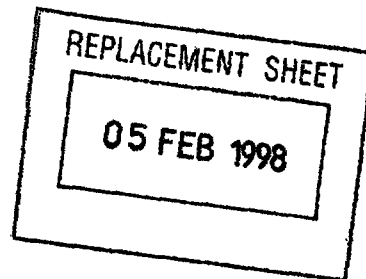


TABLE 2
SELECTIVITY AND ACTIVITY RESULTS*

Regen. No.	Temp. °F	Hours	O ₂ Level %	Pressure psig	Before Regen.			After Regen.			Hours on Stream ^(1,2,4) Producing BZ
					Hexane Conv.	Product wt. % BZ	Hexane Conv.	Product wt. % BZ			
10	600	72.0	0.5	30	55	14	74	41		1200	
	630	46.7	1.0	100							
11	600	46.8	1.0	100	82	27	68	39		1200	
	630	3.6	1.0	100							
12	600	26.3	1.0	100	86	8	72	41		1700	
	630	65.3	1.0	100							
	660	119.2	1.0	100							
13	600	66.6	1.0	100	59	24	98	39		1000+ ⁽³⁾	
	630	24.9	1.0	100							
	660	30.9	1.0	100							
	680	43.9	1.0	100							
0	Fresh Catalyst at 21 Hrs. on Stream				98 ⁽¹⁾	42 ⁽¹⁾					

*Conversion Conditions: 30 psig, WHSV = 0.72, Catalyst Temp. 880°F to 1000°F

⁽¹⁾Utilizing Feed B (Table 3)

⁽²⁾At constant (40%) aromatization activity.

⁽³⁾Utilizing Feed A (Table 3)

⁽⁴⁾BZ = Benzene

⁽⁵⁾Run was voluntarily terminated; catalyst remained active.

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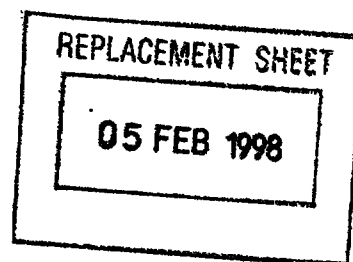


TABLE 3

FEED COMPOSITION

<u>COMPOUND</u>	FEED A	FEED B
	LIGHT NAPHTHA	MODEL FEED
	<u>wt. %</u>	<u>wt. %</u>
Total C ₃	16.1	0.0
Total C ₆	49.7	70.0
Total C ₇ -	34.2	24.0
N-C ₆	12.5	70.0
Methyl Cyclohexane	5.9	6.0

Feed A used for start of run.

Feed B used for regeneration studies.

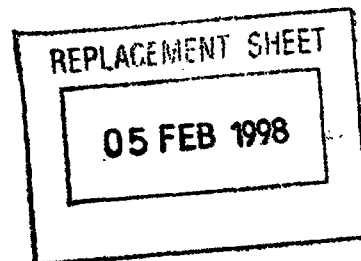
EXAMPLE XIV

Effect of Raising Temperature After
Substantially Completing Carbon Burn at Low Temperatures

This example shows that temperature may be raised beyond the 780°F limit after substantially completing a halogen-free carbon burn regeneration at lower temperatures. A platinum on barium exchanged L-zeolite catalyst was used to reform a light naphtha feedstock very similar to the one shown in Table 1 of the specification. At the end of the run, the catalyst was regenerated as follows.

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The naphtha feed was stopped. The reactor was cooled to 500°F while adding makeup hydrogen. After reaching 500°F, the unit was purged with nitrogen gas to remove substantially all of the hydrogen. Any remaining liquid hydrocarbons were drained from the gas liquid separator and other low points in the system. The nitrogen makeup rate was then reduced to a low level, the sulfur converter/sorber was by-passed, and the pressure and recycle gas rate were adjusted to about 85 psig and 1000 GHSV, respectively.

After purging the recycle loop with nitrogen, air was added through a mass flowmeter to bring the reactor inlet oxygen concentration to 0.5%. After holding for two hours at 500°F, the temperature was raised 25°F/h to 760°F while the inlet oxygen level was maintained between 0.4 and 0.6%. The temperature was then held overnight at 760°F with the inlet oxygen level between 1.0 and 1.3%.

After 16 hours at 760°F, the carbon burn was substantially complete as indicated by the difference between inlet and oxygen concentrations which was less than 0.05%. The temperature was then raised to 850°F and maintained at 850°F for 14 hours. A small amount of additional burning occurred at the high temperature but at a very low rate.

The reactor was then purged with nitrogen and a fresh recycle gas dryer brought on-line while the reactor cooled to 500°F. When the water level in the reactor effluent was less than 100 ppm, catalyst reduction was initiated by pressuring from 85 to 100 psig with hydrogen. The nitrogen makeup gas was stopped and pressure was maintained at 100 psig by adding hydrogen makeup gas. The temperature was held at 500°F for two hours and then raised 10°F/h to 900°F.

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Feed was reintroduced and the reforming reaction was resumed at the same conditions used in our previous examples and temperature was adjusted to maintain 42 wt. % aromatics in the liquid product. After 1070 hours on-stream, a least-squares plot was made of the data from 186 to 1070 hours. From this plot, it was determined that the start-of-run temperature was 868°F/h and the fouling rate was 0.020°F/h, which compares to 850°F and 0.026°F/h, respectively, for fresh catalyst. The projected run length was 3350 hours compared to 3300 for fresh catalyst. The regeneration was not as good as those of the previous examples where temperature was kept below 780°F but was considered acceptable.

As can be seen by this Example, there was no improvement in catalyst performance obtained by raising temperature of the oxygen after substantially completing the carbon burn at a temperature below 780°F.

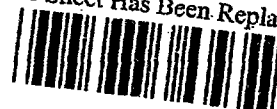
EXAMPLE XV

Regeneration with up to 520 ppm Water in the Recycle Gas

This experiment shows that up to 520 ppm water can be present in the recycle gas and still achieve an acceptable regeneration. It is, therefore, possible although not preferred to use wet air for the regeneration. Also, one may consider using a less expensive dessicant than molecular sieves in the recycle gas dryer, such as silica-gel or activated alumina.

The catalyst from Example II was regenerated a second time as follows. Preparations for the carbon burn were the same

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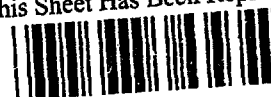
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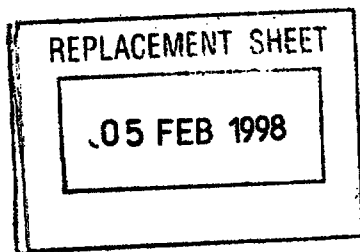
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as above. Before adding air, water was added to the recycle gas stream by bubbling makeup nitrogen through water contained in a small bomb. The makeup nitrogen feed rate was adjusted to obtain about 500 ppmv water in the gas stream entering the reactor and air was added to bring the oxygen level to 0.5%. During the carbon burn, the reactor inlet oxygen level was maintained between 0.4 and 0.6 and the inlet water level between 420 and 520 ppmv by adjusting the air and nitrogen feed rates.

After holding for two hours at 500°F, the temperature was raised 25°F/h to 700°F while maintaining inlet oxygen levels between 0.4% and 0.7%. The temperature was then held 20 hours at 700°F with the inlet oxygen level rising from 0.6 and 1.2%. The air was then shut off and dry makeup nitrogen was substituted for water-saturated nitrogen. A fresh dryer was put on-line and the reactor was cooled to 500°F.

When the water level in the reactor effluent was less than 100 ppm, the catalyst was reduced and the reforming reaction resumed as in the previous example. After 600 hours on-stream, the start-of-run temperature and fouling rate were calculated to be 875°F and 0.0186°F, respectively. This corresponds to a projected run length of 3225 hours, which is close to that of fresh catalyst.

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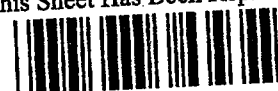
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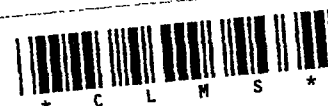
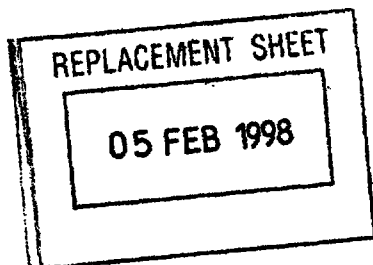


WHAT IS CLAIMED IS:

1. A process for regenerating a coke-contaminated reforming catalyst comprising platinum on a molecular sieve, said process comprising of:
 - (a) contacting said catalyst in a catalyst zone with a halogen-free oxygen-containing gas at a temperature of less than 780°F, said gas having a water content of less than about 1000 ppmv; and
 - (b) oxidizing at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the catalyst aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle.
2. A process for regenerating a coke-contaminated reforming catalyst comprising platinum on a molecular sieve, said process comprising of:
 - (a) contacting said catalyst in a catalyst zone with a halogen-free oxygen-containing gas at a temperature of less than 780°F, said gas having a water content of less than about 1000 ppmv;
 - (b) oxidizing at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the catalyst aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle;

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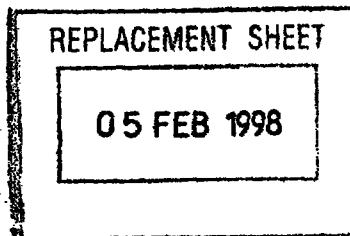


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- (c) passing at least a portion of said combustion gas through a dryer to produce a dried gas having a water content less than said portion of combustion gas; and
 - (d) recycling at least a portion of said dried gas to said catalyst zone.
3. A process for regenerating a coke-contaminated reforming catalyst comprising platinum on a molecular sieve, said process comprising of:
- (a) contacting said catalyst in a catalyst zone with a halogen-free oxygen-containing gas at a temperature of less than 780°F, said gas having a water content of less than about 1000 ppmv;
 - (b) oxidizing at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the catalyst aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle;
 - (c) passing at least a portion of said combustion gas through a dryer to produce a dried gas having a water content less than said portion of combustion gas;
 - (d) recycling at least a portion of said dried gas to said catalyst zone; and
 - (e) reducing the regenerated catalyst by contacting the catalyst with a gaseous stream containing

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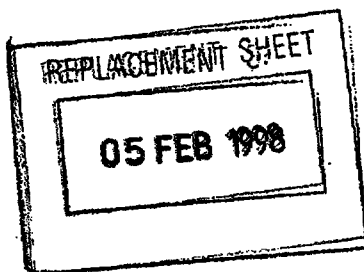
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hydrogen at an initial temperature from 300°F to 700°F.

4. The process as recited in Claim 1, 2 or 3 wherein the oxygen content of the oxygen containing gas is from between about 0.1 to about 21.0 mole % oxygen.
5. The process as recited in Claim 1, 2 or 3 wherein the oxygen content of the oxygen containing gas is from about 0.2 to about 4.0 mole %.
6. The process as recited in Claim 1, 2 or 3 wherein the molecular sieve is a large-pore zeolite.
7. The process as recited in Claim 6 wherein the large-pore zeolite is selected from the group consisting of type-X, type-Y, beta zeolite, and mordenite.
8. The process as recited in Claim 6 wherein the large-pore zeolite is type-L zeolite.
9. The process as recited in Claim 1, 2 or 3 wherein the molecular sieve is silicalite.
10. The process as recited in Claim 6 wherein the zeolite further comprises an alkaline earth metal.
11. The process as recited in Claim 6 wherein the zeolite further comprises boron.
12. The process as recited in Claim 1, 2 or 3 wherein said catalyst is bound with a support matrix comprising alumina, silica or mixtures thereof.

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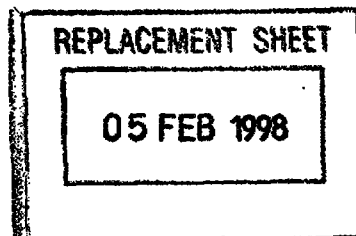
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13. The process as recited in Claim 3 further comprising raising the temperature of the gaseous stream containing hydrogen to between 800°F and 1000°F to complete the dryout and reduction.
14. The process as recited in Claim 3 wherein the carbon burn is initiated at a temperature of less than 500°F.
15. The process as recited in Claim 14 wherein the temperature is escalated during the carbon burn in a slow ramping fashion.
16. The process as recited in Claim 14 wherein the temperature is escalated during the carbon burn in a stepwise fashion.
17. The process as recited in Claim 1, 2 or 3 wherein the peak catalyst temperature during the carbon burn step is between 600°F and 750°F.
18. The process as recited in Claim 3 wherein prior to reducing the catalyst, the catalyst is purged with an inert gaseous stream.
19. The process as recited in Claim 3 further comprising:
 - (a) passing at least a portion of said gaseous stream containing hydrogen through a dryer; and
 - (b) recycling a portion of said gaseous stream containing hydrogen to said catalyst zone.
20. The process as recited in Claim 3 further comprising reducing the regenerated catalyst by contacting the

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catalyst with a gaseous stream containing a mixture of inert gas and hydrogen at a temperature between 900°F and 1000°F.

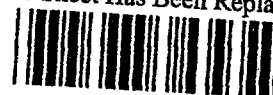
21. The process as recited in Claim 3 further comprising reducing the regenerated catalyst by contacting the catalyst with a gaseous stream containing a mixture of nitrogen and hydrogen at a temperature between 900°F and 1000°F.
22. The process as recited in Claim 21 wherein the mole ratio of nitrogen gas to hydrogen gas is at least 4:1.
23. A process for regenerating a coke deactivated reforming catalyst, comprising:
 - (a) contacting a coke-contaminated L-zeolite catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780°F, said gas having a water content between 100 and 1000 ppmv;
 - (b) oxidizing at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the aromatization activity of the L-zeolite catalyst is restored within 20°F of the activity said catalyst possessed at the start of the previous run cycle;
 - (c) passing at least a portion of said combustion gas through a dryer to produce a dried gas having a water content less than said portion of combustion gas;

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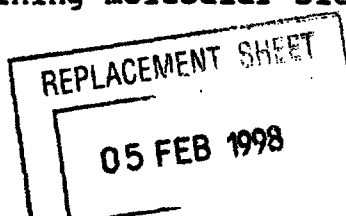


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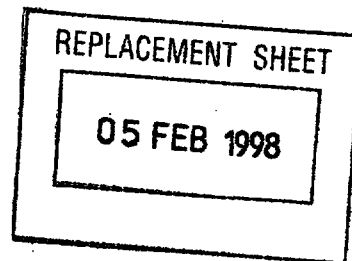
- (d) recycling at least a portion of said dried gas to said catalyst zone; and
 - (e) reducing the regenerated catalyst by contacting the catalyst with a gaseous stream containing hydrogen at an initial temperature from 300°F to 700°F.
24. The process as recited in Claim 23 further comprising the step of purging the catalyst resulting from step (b) with a gaseous stream comprising nitrogen prior to the reduction step (c).
25. The process as recited in Claim 23 further comprising the step of purging the catalyst resulting from step (b) with a gaseous stream comprising nitrogen prior to the reduction step (c) and changing the recycle gas dryer so as to reduce carbon dioxide in the recycle gas to less than 100 ppm.
26. The process as recited in Claim 23 wherein the L-zeolite catalyst contains barium.
27. A reforming process wherein a reforming catalyst is regenerated for at least two cycles by the process as recited in Claim 1, 2, 3 or 23.
28. The process as recited in Claim 1, 2, 3 or 23 wherein the catalyst is continuously withdrawn from reactors for regeneration in a separate vessel, and returned to the reactors.
29. A reforming process comprising contacting a hydrocarbon feed with a platinum containing molecular sieve



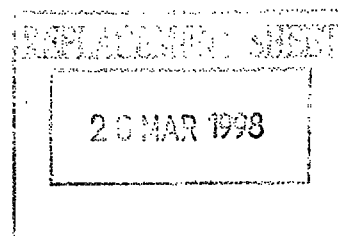


catalyst under reforming conditions and regenerating
said catalyst in accordance with the process of
Claim 1, 2 or 3.

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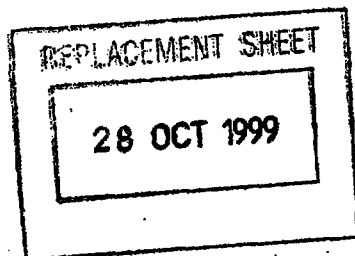
LOW TEMPERATURE REGENERATION OF COKE DEACTIVATED
REFORMING CATALYSTS

ABSTRACT

A process for generating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780°F for a sufficient period of time such that the aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle.

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REPLACEMENT SHEETS		SC
☒ Description :	paged .1. to paged .41.	
☒ Claim(s) :	paged .42. to paged .47.	
☐ Drawing(s) :	paged to paged	
☒ Abstract :	paged .48. to paged	
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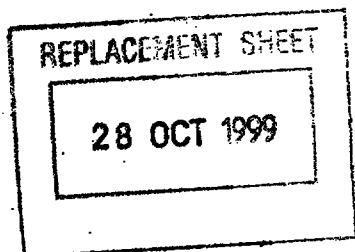
LOW TEMPERATURE REGENERATION OF COKE DEACTIVATED REFORMING CATALYSTS

BACKGROUND OF THE INVENTION

The subject of the present invention is a process for the regeneration of a hydrocarbon reforming catalyst which has been deactivated due to buildup of carbonaceous material on the catalyst. More specifically, the present invention provides a method for regenerating a coke deactivated reforming catalyst by a controlled low temperature carbon-burn procedure which results in the catalyst having activity, selectivity and stability characteristics approximating, or which are even better than, the catalyst prior to the buildup of carbon. The reforming catalysts intended to be regenerated by the process of the present invention comprise a molecular sieve material and platinum.

Platinum containing catalysts are widely used in the oil refining and petrochemical industries, and are particularly important in a reforming process where paraffins, olefins and naphthenes are converted to aromatic compounds. Conventional reforming catalysts typically include one or more metals, most typically platinum, dispersed on a base, and may also include a binding agent for adding physical support to the base, and chloride to provide an acidic function. Typically, the catalyst base is alumina, but recently molecular sieve based catalysts have been found to be effective for reforming reactions.

Catalytic compositions containing zeolites are well known in the industry and recently the use of L-zeolites in combination with other specified catalytic components have been found to be particularly preferred for reforming. The



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aromatic compounds produced by such a catalytic conversion are valuable to a refiner due to their higher octane rating, and may be recovered from the reforming product for further processing and reaction in the petrochemical industries. The L-zeolite catalysts are particularly effective for converting C₆ and C₇ non-aromatic hydrocarbons which normally boil between 52°C and 107°C (125°F and 225°F), to benzene and toluene.

In the reforming process, a hydrocarbon feedstock is passed through a catalyst-containing reactor in the presence of hydrogen at an elevated temperature. In the reactor and upon contact with the reduced or activated catalyst, some of the paraffins, olefins and naphthenes in the feedstock react to form a more desired, higher octane aromatic product. In the course of typical reforming operations, the catalysts will typically become deactivated due to the deposition of carbonaceous material or "coke" upon the catalyst, and/or sintering or poisoning of the catalytic metal particles. In commercial practice, the deactivated catalyst will then be regenerated by a process which may include as a step the exposing of the catalyst to an oxygen containing gas at elevated temperature (typically 510°C (950°F) final burn temperature) to burn the carbonaceous deposits accumulated on the catalyst. However, prior to our present invention, burning the coke off the catalyst at elevated temperatures caused the catalytic metal to agglomerate, which significantly lowered the activity and thus worsened the performance of the catalyst. Consequently, specific steps directed to the redispersion of the catalytic metal on the base were necessary. The redispersion steps typically comprise contacting the catalyst with a chloride containing gas in the presence of oxygen and water vapor, and are well known in the art.

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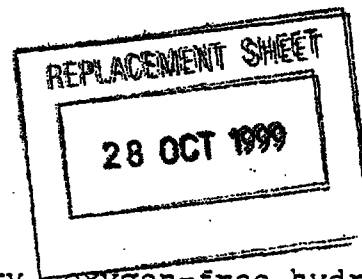
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In U.S. Patent No. 4,493,901 issued January 15, 1985 to Bernard et al., a method of regenerating a catalyst comprising platinum and a non-acidic L-zeolite is described, whereby the catalyst is subjected to a multi-step process, the first step being exposure to a hydrogen environment, followed by a carbon burn step, and then a calcination step followed specifically by an oxychlorination step. The regeneration method of Bernard et al. utilizes a hydration step following the oxychlorination step. In the hydration step, a quantity of water is added to the cooling air.

In U.S. Patent No. 4,810,683, issued March 7, 1989, to Cohn, a method is described which utilizes a halogen or halogen containing gas during the carbon burn step. The burning step of the process of U.S. Patent No. 4,810,683 occurred necessarily in the presence of a halogen or halogen containing gas and at a temperature of from 300°C to 600°C.

U.S. Patent No. 3,986,982, issued October 19, 1976, to Crowson et al., describes a method for regenerating a deactivated platinum group metal-loaded zeolites by burning off deposits on the catalyst with a stream of inert gas and oxygen at a temperature controlled to a maximum of 550°C. Example 1 shows a stepwise burn procedure to 530°C. The water content was held at 100-130 ppm. This was followed by treating with a stream of an inert gas containing from 0.5 to 20.0 vol% oxygen and from 5 to 500 ppmv chlorine as chlorine gas. The resultant catalyst is purged to remove residual oxygen and chlorine and then reduced with hydrogen.

U.S. Patent No. 4,359,400, issued November 16, 1982, to G. R. Landolt et al., describes a process whereby multimetallic platinum containing catalysts are contacted with oxygen containing gas at elevated temperatures to burn



off coke and then treated with dry, oxygen-free hydrogen halide. The catalyst is then treated with Cl_2 containing gas which is oxygen and water-free.

U.S. Patent Number 4,719,189, issued January 12, 1988 to A. S. Krishnamurthy describes a process for rejuvenating a coke-deactivated noble metal containing zeolite catalyst. The process comprises contacting the catalyst with a mixture of oxygen and sulfur dioxide, followed by catalyst reduction. Temperatures from 400°C - 449°C (752 - 840°F) are preferred.

U.S. Patent No. 4,645,751, issued February 24, 1987, to S. B. McCullen et al., describes a process for rejuvenating a highly silicious (silica-alumina ratio of at least 20) Pt zeolite catalyst wherein the Pt has become agglomerated. The agglomerated catalyst is first reduced with hydrogen. Following reduction the catalyst is treated with hydrogen chloride and oxygen in an inert gas carrier at 400 - 450°C .

U.S. Patent No. 4,752,595, issued June 21, 1988, to S. B. McCullen et al., describes a process for regenerating a noble-metal containing zeolite catalyst. The process consists of a coke burn step followed by a low temperature reduction step (100 - 250°C [212 - 482°F]). Oxidizing conditions for the coke burn include temperatures ranging from 200 - 540°C (392 - 1004°F), preferably 400 - 510°C (752 - 950°F).

U.S. Patent No. 4,657,874, issued April 14, 1987, to W. S. Borghard et al., describes a method where Pt on a highly silicious zeolite is redispersed. The process comprises a coke burn followed by oxychlorination. The oxygen burn step is done under conditions that are sufficiently mild to prevent any alteration in the crystal structure of the zeolite. Example 6 uses a temperature of

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454°C (850°F). This is then followed by treating with a stream of inert gas containing 6 to 15 Torr of chlorine gas and water vapor such the molar ratio of water to chlorine gas is between 0.01 and 2.0. Oxygen may also be present. The rejuvenation is typically carried out at 450°C (842°F).

U.S. Patent No. 4,851,380, issued July 25, 1989, to D. A. Van Leirsburg et al., describes a process for regenerating a sulfur contaminated reforming catalyst. The process includes a platinum agglomeration step which can be accomplished by contacting the catalyst with O₂ between 427°C and 649°C (800°F and 1200°F) and an oxychlorination step. Pt redispersion by contacting an agglomerated catalyst with carbon monoxide and a sulfur free halogen acid gas.

U.S. Patent No. 4,855,269, issued August 8, 1989, to D. H. Mohr, discloses a platinum redispersion method comprising a wet oxychlorination step, followed by a nitrogen purge, followed by reduction.

U.S. Patent No. 4,914,068 issued April 3, 1990, to V. R. Cross, describes a process for the improved retention of the platinum dispersion following oxychlorination if the catalyst is cooled to 430°C or preferably less than 375°C prior to start of reduction. Coke was burned off the catalyst at 510°C prior to reduction.

U.S. Patent No. 4,600,700 discloses a process for regenerating a coke-deactivated catalytic dewaxing platinum-Zeolite Beta catalyst.

WO-A-9215654 discloses a process for regenerating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less

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than 416°C (780°F) for a sufficient period of time such that the catalyst aromatization activity is restored to within 11.1°C (20°F) of the activity said catalyst possessed at the start of the previous run cycle.

Unfortunately, the presence of halogens such as chlorine or fluorine or their compounds during regeneration results in the formation of corrosive by-products such as HCl and NH_4Cl . These compounds can cause damage to equipment used in the reforming process such as heat exchangers, liquid/gas separators and reactor internals. The halogen containing compounds and their products necessary for platinum redispersion are highly toxic as well. Therefore, it is highly desirable to have available a catalyst regeneration procedure that does not include the use of a halogen containing gas.

U.S. Patent No. 5,073,529, issued December 17, 1991 to Miller et al., describes a process for regenerating a coke-deactivated reforming catalyst. A two-step carbon burn procedure is used wherein the catalyst is initially contacted with oxygen and an inert gas at a temperature ranging from 260-371°C (500-700°F). During the second step, the catalyst is contacted with oxygen and an inert gas at a temperature ranging from 454-510°C (850-950°F).

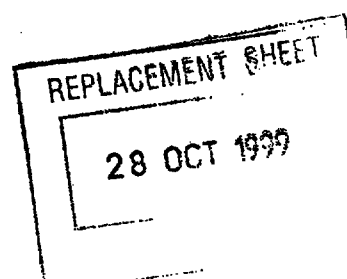
SUMMARY OF THE INVENTION

The present invention relates to a halogen-free process to regenerate a coke contaminated catalyst comprising platinum on a molecular sieve support which process comprises: (a) contacting said catalyst with a halogen-free oxygen-containing gas at a maximum temperature of less than 416°C (780°F) said gas having a water content of from 100 ppmv to 1000 ppmv and (b) oxidising at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the aromatization activity is restored to within 11.1°C (20°F) of the aromatization activity the catalyst possessed at the start of the previous run cycle. By the term "aromatization activity" we mean the extrapolated start-

of-run temperature where the run conditions and the feed as well as the aromatics yield are substantially the same as in the previous run cycle. By the practice of the present invention, the platinum on the catalyst remains sufficiently dispersed on the support to allow for an activity change of not more than 11.1°C (20°F) upon termination of the regeneration procedure, and return of the catalyst to hydrocarbon conversion service. Thus, the catalyst aromatization activity is based upon the temperature needed to achieve a desired constant aromatics production. Typically, we have controlled our process to about 40 to 42 wt.% aromatics in the product, although other values may be set, in other circumstances. Regeneration by the process of the present invention results in a catalyst which has an aromatization activity, as defined above, which is within 11.1°C (20°F) of the temperature needed in the previous run to achieve the same constant aromatics production.

Among other factors, we have found that by limiting the ultimate temperature in the carbon burn regeneration procedure to a maximum temperature of less than 416°C (780°F), preferably between 316°C to 400°C (600°F to 750°F) the catalyst may be restored to an activity very close to that of the fresh catalyst, without requiring a metal re-dispersion step. It is further preferred the carbon burn be initiated at a temperature of less than about 260°C (500°F). The recycle gas is dried to achieve a water concentration in the recycle gas of from 100 ppmv to 1000 ppm water, prior to the recycle gas entering the reforming reactor train.

We have found that by avoiding addition of a halogen or halogen containing gas during or after the carbon burn procedure, plant deterioration due to stress cracking and corrosion is minimized. Further, prior to our present invention, it was common practice to circulate soda ash or morpholine solutions through effluent heat exchangers,



transfer lines, and liquid-gas separators during the regeneration of reforming catalyst in order to prevent corrosion due to chlorides. The need to use corrosion inhibitor solutions is eliminated when regenerating reforming catalyst by the method of the present invention.

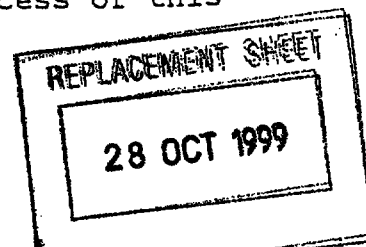
In general, the art teaches away, i.e., describes high temperature burn procedure followed by redispersion step or, burn/redispersion combined. We have now, surprisingly, found that if the coke burn and reduction are both done at low temperatures and with low concentration of water, the regenerated catalyst has excellent activity and unexpectedly long life.

Surprisingly, we have also found that the rate of deactivation or "fouling rate" of the regenerated catalyst decreases following the application of the regeneration process of the present invention. Thus, a catalyst regeneration procedure was discovered in which noble metal does not appreciably agglomerate; eliminating the need for a redispersion step, which are among the advantages of using the present regeneration method on a Pt containing molecular sieve type catalyst.

DETAILED DESCRIPTION OF THE INVENTION

As explained in the summary section above, the present invention is a procedure for regenerating reforming catalysts, comprising platinum on a L-zeolite or silicalite molecular sieve support.

By the term "reforming" we mean the process of converting paraffins, naphthenes or olefins to aromatic hydrocarbons via hydrodecyclization or dehydrogenation. Feeds useful in reforming typically include hydrocarbons having from six to eleven carbon atoms, but these feeds can also include narrower cuts, such as a C₆ to C₇ cut. Indeed, the reforming catalysts that can be regenerated by the process of this



invention can be used to make chemicals as well as gasoline components. For example, benzene, toluene or mixtures thereof can be produced by reforming hydrocarbons having six to seven carbon atoms.

The catalysts advantageously regenerated by the method of this invention comprise platinum on a L-zeolite or silicalite molecular sieve support. Molecular sieves are defined as porous materials which exhibit the property of acting as sieves on a molecular scale.

Silicalite is an example of a molecular sieve composed of substantially silica. Silicalite has the same crystal structure as ZSM-5 except that substantially all of the aluminum atoms have been replaced with silicon atoms.



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Catalyst Description

In copending Application US-A-5052561,
assignee of the present invention

assigned to the

an intermediate pore size crystalline silicate having a silica to alumina ratio of preferably at least 500, is described. We have found the present catalyst regeneration process may be advantageously used to regenerate the intermediate pore size crystalline silicate catalyst, and that the present process may also be advantageously applied to a mixed catalyst system comprising the intermediate pore size crystalline silicate described in copending Application US-A-5052561.

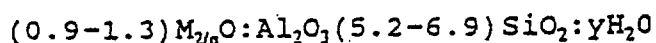
A preferred catalyst to regenerate by the process of this invention comprises platinum on an alkaline earth or alkali metal exchanged, L-zeolite. It is especially preferred that this catalyst be protected from sulfur poisoning during its use in reforming, so that the catalyst is never contacted with more than 100 ppb by weight sulfur in the feed. This can be accomplished by using a sulfur converter/sorber system as described in U.S. Patent No. 4,925,549 to Robinson et al. The regeneration process of this invention is especially effective on substantially sulfur free catalyst.

In addition to platinum, the catalysts regenerated by the present invention may contain elements such as rhenium, tin, germanium, iridium, copper, iron, cobalt, nickel, and titanium which in certain cases may improve catalyst selectivity or stability. For naphtha reforming, it is desirable that the molecular sieve catalyst have a low acidity. Acid sites may be neutralized by ion exchange with alkali ions such as lithium, sodium, potassium, cesium and rubidium ions or alkaline earth ions such as calcium,

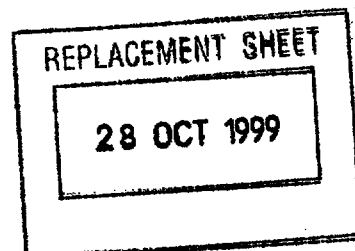
magnesium, strontium, and barium. With zeolites, low acidity may also be achieved by substituting boron for aluminum in the zeolite framework; for example, boron-substituted beta zeolites or by using a zeolite with a silica/alumina ratio greater than 500.

The present invention has been found to be particularly effective when applied to L-type zeolites, which are large-pore zeolites. Large-pore zeolites are defined as zeolites having an effective pore diameter of between 0.6 and 1.5 nm (6 and 15 Angstroms).

A typical composition of L-type zeolites, expressed in terms of mole ratios of oxides, may be represented as follows:



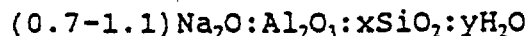
wherein M designates a cation, n represents the valance of M, and y may be any value from 0 to 9. Zeolite L, its X-ray diffraction pattern, its properties and method for its preparation are described in detail in U.S. Patent No. 3,216,789 which is hereby incorporated by reference. The true formula may vary without changing the crystalline structure. For example, the mole ratio of silicon to aluminum (Si/Al) may vary from over a range which is typically 1.5 to 3.5, but may be higher. The barium exchanged form of zeolite L is particularly preferred as described, for example, in U.S. Patent Nos. 4,434,311 and 4,547,472.



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The chemical formula for zeolite Y expressed in terms of oxide molar ratio may be written as:

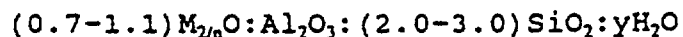


wherein x is a value between 3 and 6, and y may be a value up to 9. Zeolite Y has a characteristic X-ray diffraction pattern which may be employed with the above formula for identification. Zeolite Y is described in more detail in U.S. Patent No. 3,130,007. U.S. Patent No. 3,130,007

shows a zeolite useful in the present invention.

More recent patents disclose high silica/alumina versions of zeolite Y produced by steaming and/or chemical extraction which removes aluminum from the framework of the originally synthesized zeolite. Y-zeolites with framework silica/alumina ratios as high as 50:1 or higher may be prepared by these methods, and are useful supports for the reforming catalysts regenerated by the method of the present invention.

Zeolite X is a synthetic crystalline zeolitic molecular sieve which may be represented by the formula:



wherein M represents a metal, particularly alkali and alkaline earth metals, n is the valence of M, and y may have any value up to about 8 depending upon the identity of M and the degree of hydration of the crystalline zeolite.

Zeolite X, its x-ray diffraction pattern, its properties and method for its preparation are described in detail in U.S. Patent No. 2,882,244,

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which shows a zeolite useful in the present invention.

Zeolite beta is a known synthetic crystalline aluminosilicate originally described in U.S. Patent Nos. 3,308,069 and RE 28,341 to which reference is made for further details of this zeolite, its preparation and properties. These references describe the composition of zeolite beta in its as-synthesized form as follows:

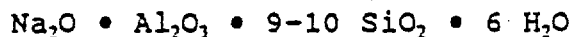


where X is less than 1, preferably less than 0.75, TEA represents tetraethylammonium ion, Y is greater than 5 and less than 100, and W is up to 4, depending on the condition of dehydration and on the metal cation present. These references also teach that the sodium ion may be replaced by another metal ion using ion exchange techniques. Subsequent publications such as European Patent Applications Nos. 95,304; 159,846; 159,847; and 164,939 have broadened the definition of zeolite beta to include materials prepared using templating agents other than tetraethylammonium hydroxide and materials having a Si/Al ratio greater than 100. Also the zeolite described in European Patent Application No. 55,046 ("Nu-2") and British Patent Application No. 2,024,790 ("Borolite B") have structures and X-ray diffraction patterns similar to that of zeolite beta and are included within the scope of the term "zeolite beta" as used herein.

Mordenite is a commercially available zeolite which occurs in nature and has also been synthesized. Both "small port" and "large port" mordenites have been synthesized. The "large port" form is preferred for catalysis and is

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described in "Zeolite Molecular Sieves" by Donald W. Breck, published by John Wiley and Sons. A typical oxide composition is:



The silica/alumina ratio may be increased by extracting alumina using various chemical and thermal methods similar to those employed with zeolite Y.

The percentage of platinum in the catalyst is between 0.1% and 10%, the lower limit corresponding to minimum practical catalyst activity and the upper limit to roughly the maximum possible platinum utilization. Preferably, the catalyst contains between 0.2 and 5.0 percent platinum. Group VIII metals are introduced into a large-pore zeolite during synthesis, impregnation or ion exchange in an aqueous solution of an appropriate metal salt. If it is desired to introduce two Group VIII metals onto the large-pore zeolite, the operation may be carried out simultaneously or sequentially.

By way of example, platinum can be introduced by impregnating the large-pore zeolite with an aqueous solution of tetrammineplatinum (II) nitrate $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, tetrammineplatinum (II) chloride $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, or diammineplatinum $[\text{Pt}(\text{NH}_3)_2](\text{NO}_2)_2$. In an ionic exchange process, platinum can be introduced by using cationic platinum complexes such as tetrammineplatinum (II) nitrate.

A binder may be used in the preparation of the catalysts. An inorganic oxide is used as a matrix to bind the large-pore zeolite. This binder can be a natural or a synthetically produced inorganic oxide or combination of

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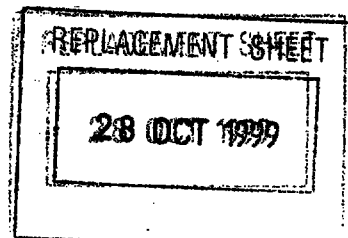
inorganic oxides. Typical inorganic oxide binders which can be used include clays, alumina, silica or mixtures thereof. Preferable binders are alumina, silica, or mixtures thereof. Acidic sites on the binder are preferably exchanged by cations which do not impart strong acidity (such as sodium, potassium, rubidium, cesium, calcium, strontium or barium).

After the desired metal or metals have been introduced, the catalyst is typically calcined in air and then reduced in a hydrogen environment.

The regeneration process of the present invention may be useful on catalysts in the physical form of extrusions, spheres, pills, pellets, granules, broken fragments, or various other shapes known in the art.

Catalyst Use and Contamination

The reforming catalysts regenerated by the process of the present invention are used for aromatization of C_6 to C_{11} , preferably C_6 and C_7 non-aromatic hydrocarbons. Accordingly, a hydrocarbon feedstream which comprises a C_6 to C_{11} paraffin, olefin, or naphthene, is contacted with the catalyst at aromatization conditions. Aromatization conditions typically include an absolute pressure of from 50.7 to 5070 kPa (0.5 to 50.0 atmospheres), with the preferred pressure being from 101 to 1010 kPa (1.0 to 10.0 atmospheres), a temperature of from 427 to 649°C (800 F to 1200°F), preferably 427°C to 570°C (800°F to 1050°F), and a liquid hourly space velocity of from between 0.1 to 10 per hour. Preferably, hydrogen is employed in the process. When present, hydrogen may be circulated at a rate of from 1.0 to 10.0 moles of hydrogen per mole of hydrocarbon in the hydrocarbon feedstream. Feed streams entering the reforming reactors



should be low enough in sulfur and water to prevent catalyst deactivation by sulfur poisoning or platinum sintering.

Catalyst Regeneration Method

The gradual accumulation of coke and other deactivating carbonaceous deposits on the catalyst will eventually reduce the activity of the catalyst and selectivity of the aromatization process. Typically, catalyst regeneration becomes desirable when from 0.5 to 3.0 wt. % or more of carbonaceous deposits are laid down upon the catalyst. At this point, it is typically necessary to take the hydrocarbon feedstream out of contact with the catalyst and purge the hydrocarbon conversion zone with a suitable gas stream. The catalyst regeneration method of the present invention is then performed either by unloading the catalyst from the conversion zone and regenerating in a separate vessel or facility or performing regeneration in-situ. Alternatively, the catalyst may be continuously withdrawn from the reactor for regeneration in a separate vessel, to be returned to the reactor as in a Continuous Catalytic Reformer.

In fixed bed operation, it may sometimes be necessary to dump the catalyst from the reactors and screen out fines in order to reduce pressure drop. This typically occurs after several years of operation. The dump and screen procedure is usually done in combination with a catalyst regeneration. First carbon is burned off the catalyst following the procedures of this invention. This also serves to reoxidize finely divided metals on the catalyst such as iron and platinum. In their metallic form, these metals will rapidly oxidize when exposed to air and possibly ignite a fire or explosion when hydrocarbons are also present.

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The catalyst is then dumped from the reactors into a screening device where the fines are removed. It is then reloaded into the reactors and dried by circulating nitrogen through the reactors and recycle gas dryer while heating to reduction temperature. When water levels in the reactor effluent are sufficiently low, the catalyst is then reduced according the procedures of this invention and returned to reforming service. The dryout time can be shortened and the catalyst protected from water, carbon dioxide, and sulfur compounds in the atmosphere by blanketing with nitrogen or dry air during the dumping, screening, and reloading processes.

According to the catalyst regeneration method of the present invention, the essential step of the method incorporates a lower temperature carbon burn step. The lower temperature carbon burn step involves contacting the deactivated catalyst with a gaseous mixture of oxygen and an inert gas. The oxygen is typically derived from air and an inert gas serves as a diluent, such that oxygen concentration is from about 21 mole % oxygen to a lower limit which for the practice of the present invention may be as low as 0.1 mole % oxygen. The practice of the present invention is not limited to use of air, however, and higher levels of oxygen may be used in methods where oxygen is supplied in a more pure form such as from cylinders or other containing means. Typical inert gases useful in the low temperature carbon burn step may include nitrogen, helium, carbon dioxide, and like gases or any mixture thereof; nitrogen being preferred. The regeneration gases should be substantially sulfur-free as they enter the reactor, and contain from 1000ppmv to 1000ppmv water. Because the oxygen content determines the rate of burn, it is desirable to keep the oxygen content low so as

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not to damage the catalyst by overheating and causing metal agglomeration, while still conducting the carbon burn step in a manner that is both quick and effective. We have found it desirable to keep the oxygen level in the inlet to the regeneration vessel between 0.2 to 4.0 mole % during the practice of the present invention to avoid thermal damage to the catalyst, and still allow for the regeneration process to be accomplished in a reasonable amount of time.

The low temperature carbon burn process of the present regeneration method occurs at a temperature of between 149°C to 416°C (300°F to 780°F). Other conditions present during the low temperature carbon burn step include a pressure sufficient to maintain the flow of the gaseous oxygen containing mixture through the catalyst zone such as a pressure of between 101 to 5070 kPa (1.0 to 50.0 atmospheres) and preferably from 203 to 1520 kPa (2 to 15 atmospheres), and a gas hourly space velocity of 100 to 10,000 per hour, with a preferred value of 500 to 5,000 per hour.

The regeneration method of the present invention is performed in a halogen-free environment. By halogen-free, we mean that chlorine, fluorine, bromine, or iodine or their compounds including for example, hydrogen chloride, carbon tetrachloride, ethylene dichloride, propylene dichloride; are not added at anytime during the catalyst regeneration process.

It is desirable to keep water levels low during the reforming reactions and during the regeneration procedure. This is especially true when temperatures are above 371°C (700°F). Although short periods of time (several minutes) at water levels as high as saturation can be tolerated at 371°C (700°F) and higher, it is desirable to avoid this high a water level.

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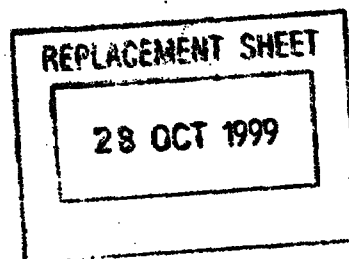
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A preferred embodiment of the present invention includes the use of a dryer in combination with flowing at least a portion of the combustion gas resulting from the contacting of the catalyst with the oxygen containing gas to a dryer and recycling the dried combustion gas to the catalyst zone. We have found that drying the recycle gas further reduces catalytic metal agglomeration, resulting in a more active regenerated catalyst. Water in the recycle gas is reduced to from 100 ppmv to 1000 ppmv,

prior to the gas being recirculated to the catalyst zone. We have found results to be best when a fresh dryer is employed just prior to the beginning of and throughout the coke-burn step.

In the preferred embodiment of the present invention, the low temperature carbon burn step results in removing most of the carbonaceous material from the catalyst while leaving an amount of from between 0.1 to 0.5 wt. % carbon on the catalyst. Although the present invention is not limited by any theory of operation, one possible explanation of the resulting improved catalyst performance is that the small amount of carbon remaining on the catalysts locates at the acid sites, and thus significantly decreases the fouling rate of the regenerated catalyst. Surprisingly, we have also found the yield of C₃+ product to increase slightly after a first regeneration of the catalyst.

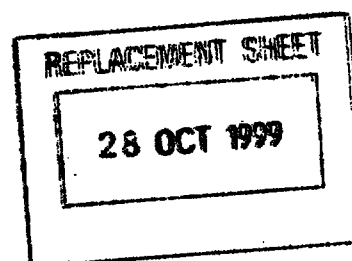
Further, in another preferred embodiment of the present invention, the first reactor inlet temperature is increased during the carbon burn in a step-wise fashion over a period of about one to five days from an initial temperature of less than 260 °C (500°F), preferably between 149°C and 260°C (300°F and 500°F) to achieve a final peak catalyst bed temperature of less than 416°C (780°F), preferably between about 316°C and 400 °C (600°F and 750 °F).



The oxygen concentration at the first reactor inlet should be controlled in the process of the present invention so as to limit exotherms and high moisture levels due to hydrocarbon combustion. Therefore, in the practice of a preferred embodiment of the present invention, the oxygen is maintained at a level between 0.2 mole % and 2.0 mole % in the oxygen containing gas throughout the carbon burn-off step. During the initial stages of the burn, it is preferred the oxygen level be maintained at a level between 0.2 and 0.5 mole %. As the rate of burn subsides, oxygen levels may be increased to between 0.5 and 4.0 mole %.

The resulting regenerated catalyst with a portion of carbonaceous material burned off is thereafter typically cooled to about 260°C (500°F) and purged with nitrogen or another inert gas to displace the oxygen and any water therefrom. The exit gas is easily monitored to determine when the catalyst zone is substantially free of oxygen and water.

After the low temperature carbon burn-off and purge, the catalyst is activated by treatment with hydrogen. In the initial reduction step, the catalyst is contacted with a hydrogen containing stream at a temperature of from 149°C to 371°C (300°F to 700°F) for a period of at least of 0.1 to 10.0 hours. Preferred conditions for the reduction step are from 204°C to 316°C (400°F to 600°F) for a period from 0.1 to 2.0 hours. The pressure and gas rates utilized in the reduction step are preferably very similar to those above described in the low temperature carbon burn step. Following the initial reduction, the catalyst may be further reduced and dried by circulating a mixture of inert gas and hydrogen while raising the temperature to between 480 and 540°C (900 and 1000°F). In the reduction step, metallic components



are returned to their elemental state and the resulting regenerated catalyst possesses activity, and selectivity characteristics quite similar to those occurring in a fresh catalyst. Additionally, we have found the regenerated catalyst has improved stability, as measured by a decreased fouling rate. When iron oxides are present on the catalyst or in the piping, it is desirable to use at least a 4:1 mole ratio of nitrogen to hydrogen during the reduction and dryout procedure, in order to limit the formation of NH_3 to less than 200 ppmv.

After completing the reduction step, the temperature is lowered to 427°C (800°F) or less. The reforming process in which the catalyst is employed may be resumed by charging the hydrocarbon feedstream to the catalyst zone and adjusting the reaction conditions to achieve the desired conversion and product yields.

The following examples are intended to further exemplify the invention, and are not intended to limit the invention in any way.

EXAMPLES I to X, XII AND XIII are not in accordance with the present invention.

LOW TEMPERATURE REGENERATION

EXAMPLE I (for comparison only)

Pretreatment and Composition of Naphtha Feedstock

A hydrocarbon feedstock was hydrotreated and dried to remove sulfur, oxygen, and water. The treated feed was stored under nitrogen to keep it substantially free of water and oxygen. The sulfur content of the hydrotreated feed was about 0.1 ppmw. A gas chromatographic analysis showed the following composition.

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	<u>LV%</u>
i-pentane	0.0
n-pentane	0.5
2,2-dimethylbutane	2.2
2,3-dimethylbutane	3.5
2-methylpentane	17.9
3-methylpentane	14.5
n-hexane	20.0
2,2-dimethylpentane	1.3
2,4-dimethylpentane	1.7
2,3-dimethylpentane	2.8
2-methylhexane	7.5
3-methylhexane	8.5
n-heptane	4.5
C ₈ ⁺ paraffins	2.1
cyclopentane	1.2
methylcyclopentane	4.9
cyclohexane	2.0
methylcyclohexane	0.5
other C ₆ - C ₇ naphthenes	1.7
benzene	0.2
toluene	0.7
ethylbenzene	0.2
heavies	1.6

EXAMPLE II (for comparison only)First Run Cycle Starting with Fresh Catalyst

Eighty cubic centimeters of fresh reforming catalyst were charged to a one-inch diameter tubular reactor. The catalyst comprised platinum on barium exchanged L-zeolite and a binder. The reactor was installed in a naphtha reforming pilot plant inside a three-zone electric furnace. Catalyst bed temperatures were measured by six equally spaced thermocouple points located from the top to the bottom of the catalyst bed in an axial thermowell. The

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pilot plant was purged and pressure tested with nitrogen, depressured, then pressured to 786 kPa (100 psig) with a blend of 1.0 % oxygen in nitrogen and the recycle compressor started. The reactor effluent passed through a chilled liquid-gas separator, a moisture analyzer, a dryer containing 4 A molecular sieves, a compressor, a mass flowmeter, and back to the reactor. The gas circulation rate was adjusted to 0.7 standard liters per minute. A small amount of the recycle gas was allowed to bleed off the recycle loop and makeup oxygen/nitrogen blend was fed from a cylinder.

The catalyst was dried by circulating the oxygen/nitrogen blend and heating the to 260°C (500°F). The temperature was held at 260°C (500°F) until the reactor effluent contained less than 300 ppm

water. The furnace temperature was then raised to 316°C (600°F) and held until water in the reactor effluent again was less than 300 ppm. Finally, the temperature was raised to 317°C (700°F) and held until the reactor effluent contained less than 100 ppm water. The reactor was cooled to 260°C (500°F) and the oxygen/nitrogen makeup gas replaced with dry nitrogen. The pilot plant was purged of oxygen and the pressure adjusted to 579 kPa (70 psig) with the compressor continuing to operate at the same setting.

Catalyst reduction was initiated by switching the makeup gas from nitrogen to hydrogen and pressuring from 579 kPa (70 psig) up to 786 kPa (100 psig). The compressor setting was then readjusted to again obtain a circulation rate of 0.7 standard liters per minute. After holding at 260°C (500°F) for an hour, the reactor furnace reactor temperature was raised to 371°C (700°F) at rate of 27.8°C/h (50°F/h). The temperature was held at 371°C (700°F) until water in the reactor effluent was less than 300 ppmv and then raised to 427°C (800°F) at 27.8°C/h (50°F/h). When moisture in the reactor effluent again fell below 300 ppmv, the temperature was raised to

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480°C (900°F) and held until water in the reactor effluent was less than 100 ppmv. The furnace temperature was then lowered to 427°C (800°F) and preparations were made for naphtha feed introduction. This included putting a sulfur converter/sorber reactor on-line in the recycle loop between the naphtha feed introduction point and the reforming reactor. The purpose of the sulfur converter/sorber was to reduce sulfur compounds in the feed entering the reforming reactor to below 5 ppbv.

The naphtha feed from Example I was fed at a rate of 128 mL/h corresponding to a liquid hourly space velocity (LHSV) of 1.6 volumes of feed per volume of catalyst per hour. Pressure was controlled at 786 kPa (100 psig) by allowing product hydrogen gas to exit the recycle loop through a back pressure regulator. The product hydrogen stream was analyzed and the hydrogen recycle rate was adjusted to obtain a hydrogen to naphtha feed molar ratio of 3.0. Liquid product was collected in the separator at 16°C (60°F). A level control and valve allowed the separator to drain into a debutanizer still which produced a C₃⁺ liquid product.

After feed introduction, the furnace temperature was rapidly raised until the catalyst aromatization activity was able to produce a liquid product comprising 42 wt. % aromatics. The yield of liquid product was about 85 LV% on feed. Thereafter as the catalyst deactivated temperatures were raised to maintain constant aromatics in the liquid product.

In order to determine aromatization activity in terms of a start-of-run temperature, the following procedure was used. After an initial lineout period, the average catalyst bed temperature was plotted against time to determine the catalyst deactivation rate. Such plots are generally linear

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and may be fitted by the least squares method. The slope of the line is the catalyst deactivation rate and the start-of-run temperature is defined as the zero time intercept. An approximate eventual run length is estimated by making a linear extrapolation to the end of run temperature. At end of run, aromatics selectivity begins to decrease and catalyst deactivation accelerates markedly. The end of run temperature was expected to be 500°C (935°F) for the feed and run conditions above.

After startup, the pilot plant ran at constant LHSV, recycle ratio, pressure, and aromatics for 658 hours. A least squares fit of the reaction temperature data yielded a fouling rate of 0.014°C/h (0.026°F/h) and a start-of-run temperature of 460°C (855°F). Assuming an end of run temperature of 500°C (935°F), the eventual run length would have been about 3100 hours if the reaction conditions had remained unchanged.

After 658 hours on-stream, reaction conditions were changed in order to study process variable effects. The run continued under various conditions for a total of 3810 hours. At the end of the run, the naphtha feed was stopped and hydrogen circulation was continued while the reactor furnace cooled to 260°C (500°F). The unit was then purged with nitrogen and allowed to cool to ambient temperature. Finally, the reactor was blocked off under nitrogen pressure and the catalyst saved for a future regeneration.

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EXAMPLE III (for comparison only)

First Regeneration of the Catalyst

The reactor containing the catalyst from Example II was reinstalled in the pilot plant, purged with nitrogen, and heated to reaction temperature in hydrogen. The reforming reaction was then resumed at the original space velocity, pressure, and recycle ratio to determine catalytic activity. After 84 hours on stream it was determined that an average catalyst temperature of 490°C (919°F) was required to make a C₇ liquid product containing 42 wt. % aromatics. The catalyst had therefore aged 41°C (74°F) since the start of run in Example II.

Hydrogen circulation continued while the naphtha feed was stopped and the reactor furnace was cooled to 260°C (500°F). At 260°C (500°F), the sulfur converter/sorber reactor was bypassed and blocked-in and the separator drained. Recycle gas circulation continued overnight while the recycle loop was purged with nitrogen and the reforming reactor cooled to 149°C (300°F).

The carbon burn was initiated at 149°C (300°F) and 752 kPa (95 psig) by introducing air and about sixty standard cubic centimeters per minute of 1.0% oxygen/nitrogen blend to the recycle gas stream and adjusting the air flow to maintain about 1.0% oxygen in the gas entering the reforming reactor. The recycle gas rate was 1.3 standard liters per minute. The air was dried with molecular sieves and metered through a mass flowmeter. The oxygen/nitrogen blend was added to provide enough off-gas for oxygen analysis. The molecular sieve dryer remained in the recycle loop and moisture levels were measured before and after the dryer. Reactor inlet

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oxygen concentration was maintained at about 1.0% throughout the burn. Water in the reactor inlet stream was less than 5 ppmv.

Upon introducing air an exotherm equal to about 11.1°C (20°F) was obtained at the front end of the catalyst bed. This was attributed to the combustion of hydrocarbon vapors in the recycle gas. The exotherm subsided after several hours. The furnace temperature was held at 149°C (300°F) for 22 hours then raised to 260°C (500°F) at a rate of 27.8°C/h (50°F/h). As the furnace temperature was raised, the exotherm increased to about 13.9°C (25°F) and moved through the catalyst bed. The oxygen concentration in the reactor effluent dropped to zero. By the time the furnace temperature reached 260°C (500°F) the exotherm and oxygen consumption were decreasing again.

The furnace temperature was held at 260°C (500°F) for 20.0 hours then raised to 316°C (600°F) at a rate of 27.8°C (50°F) per hour. Again, the burning of catalyst coke accelerated as temperature was raised. The exotherm increased and oxygen in the reactor effluent decreased. The exotherm peaked at about 5.5°C (10°F) and oxygen conversion peaked at about 30%. A short time after the furnace temperature reached 316°C (600°F), the burning again subsided.

After holding at 316°C (600°F) for 22 hours, the furnace temperature was raised 27.8°C/h (50°F/h) to 371°C (700°F). This time the peak exotherm was less than 2.8°C (5°F). After 22.0 hours at 371°C (700°F), the air and oxygen/nitrogen blend were shut-off. The recycle gas dryer which was now loaded with water and carbon dioxide was bypassed and a fresh dryer brought on-line. Gas circulation continued while the recycle loop was purged with nitrogen and the reforming reactor was cooled to 260°C (500°F).

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Catalyst reduction was initiated at 260°C (500°F) by depressuring to 579 kPa (70 psig) and then pressuring up to 786 kPa (100 psig) with hydrogen while the compressor continued to operate. The makeup gas was switched from nitrogen to hydrogen. The temperature was held at 260°C (500°F) for one-hour and then raised 2.2°C/h (4°F/h) to 480°C (900°F). The temperature was held at 480°C (900°F) for 16 hours before cooling to 427°C (800°F) for naphtha feed introduction.

EXAMPLE IV (for comparison only)

Catalyst Performance After First Regeneration

After catalyst regeneration, the naphtha reforming reaction was resumed with the same conditions and feed used in Example II. Liquid product yields were the same as before regeneration and slightly better than with fresh catalyst. After 840 h on stream a least squares fit was made as before to determine the start-of-run temperature and deactivation rate. The start-of-run temperature was 459°C (859°F) and the catalyst deactivation rate was 0.009°C/h (0.017°F/h). Thus, the catalyst activity had been restored to within 2.2°C (4°F) of fresh catalyst. Surprisingly, the catalyst deactivation rate was significantly less than with fresh catalyst. The projected run length was 4300 hours compared to 3100 hours for the first cycle.

After determining start-of-run temperature and catalyst deactivation rate, the liquid hourly space was increased to 3.0 and the furnace temperature was increased to obtain a maximum catalyst bed temperature of 550°C (1025°F) in order to accelerate catalyst fouling. After 1464 hours at these conditions, the catalyst had reached approximately end of run activity and the liquid hourly space velocity was reduced to the original value of 1.6. The average catalyst

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bed temperature to produce a liquid product containing 42. wt. % aromatics was then determined to be 500°C (939°F). The catalyst had aged 44.4°C (80°F) from the start of the second run cycle.

EXAMPLE V (for comparison only)

Second Regeneration of the Catalyst

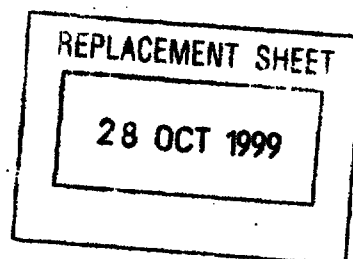
At the conclusion of the run cycle described in Example IV, the naphtha feed was stopped and the reforming reactor was cooled to 260°C (500°F) while continuing to circulate hydrogen. At 260°C (500°F), the recycle loop was purged with nitrogen, the sulfur converter/sorber was taken off-line, and the separator was drained. Purging continued while the reactor cooled to 149°C (300°F).

The catalyst was then regenerated following substantially the same procedure used in Example III.

EXAMPLE VI (for comparison only)

Catalyst Performance Following Second Catalyst Regeneration

After the second regeneration, the reforming reaction was restarted with same conditions and feed used at the start of the first and second run cycles. After 660 hours, a least squares fit was again made to determine the start-of-run temperature and catalyst deactivation rate. The start-of-run temperature was determined to be 468°C (874°F) and the catalyst deactivation rate was 0.0067°C/h (0.012°F/h). The projected run length at these conditions was therefore about 5000 hours. The start-of-run temperature had declined 7.2°C (13°F) from the start of previous run cycle, but the catalyst deactivation



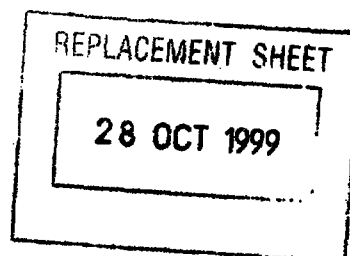
rate was again reduced so that projected run length had increased. The liquid C_3^+ yield was the same as after the first regeneration.

EXAMPLE VII

Regeneration without Dryer (for comparison only)

A coked catalyst from a 4700 hour pilot plant run was saved and later returned to service at the same conditions used in the previous examples. Prior to its use, the catalyst had the same composition as the catalyst used in Example II. After 330 hours on-stream, the average catalyst bed temperature was 500°C (930°F) and liquid product contained 42 wt. % aromatics. The yield of liquid product on feed was beginning to decline and was 85.5 LV%.

At this point the naphtha feed was stopped and the reactor cooled to 260°C (500°F) in circulating hydrogen. At 260°C (500°F), the recycle loop was purged with nitrogen and the sulfur converter/sorber reactor and recycle gas dryer were bypassed and the separator was drained. The pressure was adjusted to 683 kPa (85 psig). This time the carbon burn was started at 260°C (500°F). Air and oxygen/nitrogen blend were added to the recycle gas stream as in Examples III and V, but the oxygen content at the reactor inlet was adjusted to 0.5% instead of 1.0%. The dryer remained bypassed throughout the burn. There was complete oxygen conversion and the exotherm was about 6.7°C (12°F). After holding at 260°C (500°F) for 1.5 hours, the furnace temperature was raised 13.9°C/h (25°F/h) to 371°C (700°F). Oxygen breakthrough occurred when the furnace temperature reached about 340°C (640°F). There was only a small amount of burning by the time the furnace temperature reached 371°C (700°F) and the exotherm was negligible. Reactor inlet oxygen level was raised to 1.0%



and the temperature held at 371°C (700°F) for 20 hours to complete the burn. The exotherm during the final burn was less than 1.1°C (2°F).

Since the recycle gas dryer was bypassed, water built up in the recycle gas during the burn until it reached saturation levels in the separator. Moisture levels in the recycle gas exceeded 2000 ppm well into the 371°C (700°F) hold period.

After completing the carbon burn, the recycle loop was purged with nitrogen and the reactor was cooled to 260°C (500°F) while recycle gas circulation continued. At 260°C (500°F) the dryer and the sulfur converter/sorber were put back on line. When water in the recycle gas fell below 100 ppmv, the plant was pressured up 786 kPa (100 psig) with hydrogen to initiate catalyst reduction. After an hour at 260°C (500°F), the reactor was heated to 480°C (900°F) at rate of 5.6°C/h (10°F/h). The reactor was held at 480°C (900°F) until the moisture content of the reactor effluent was less than 100 ppm then cooled to 427°C (800°F) for feed introduction.

EXAMPLE VIII (for comparison only)

Catalyst Performance after Regenerating without a Dryer

After the catalyst regeneration in Example VII, the naphtha feed was restarted and the reforming reaction resumed for 590 hours. The feed and the run conditions were the same as in Example II. Catalyst performance was not as good as obtained in Examples II, IV, or VI. The start-of-run temperature was 464°C (868°F) and the fouling rate was 0.017°C/h (0.031°F/h). The projected run length was therefore only about 2100 hours.

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EXAMPLE IX

Regeneration with Dryer (for comparison only)

The regeneration procedure of Example VIII was repeated with another coked catalyst sample except that the recycle gas dryer was employed during the carbon burn and consequently the reactor inlet moisture levels were always less than 5 ppm. The catalyst composition prior to its use as a reforming catalyst was the same as that used in Examples II and VII.

EXAMPLE X (for comparison only)

Catalyst Performance After Regeneration with Dryer

The catalyst regenerated in Example IX was tested with the same run conditions and feed as in Example VIII. After 576 hours on-stream, the start-of-run temperature was 461°C (862°F) and catalyst deactivation rate was 0.011°C/hr (0.019°F/hr). The projected run length was 3800 hours compared to 2100 in Example VIII.

The results of from Examples I to X are summarized in Table 1 below.

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TABLE 1

<u>Description</u>	<u>Examples</u>	<u>Start of Run Temp. °C (°F)</u>	<u>Deactivation Rate °C/h (°F/h)</u>	<u>Projected Run (hours)</u>
Fresh Catalyst	II	457 (855)	0.014 (0.026)	3100
First Regeneration	II-IV	459 (859)	9.4×10^{-3} (0.017)	4100
Second Regeneration	V-VI	468 (874)	6.6×10^{-3} (0.012)	5000
Regeneration without Dryer	VII-VIII	464 (868)	0.017 (0.031)	2100
Regeneration with Dryer	IX-X	461 (862)	0.011 (0.019)	3800

The Table clearly shows that a controlled low temperature carbon-burn regeneration procedure restores most of the activity present at the start of the previous run cycle and that catalyst deactivation rates are significantly reduced, such that several cycles are possible before there is a need for platinum redispersion. The results further show the advantage in using a dryer to reduce the water content of the recycle gas during the carbon burn. These results are surprising in view of the prior art and afford the opportunity to increase cycle length and avoid the use of corrosive and sometimes highly toxic halogen compounds during regeneration.

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EXAMPLE XI

Regeneration Procedure for a Large-Scale Plant

Allowing for differences in the exotherm as compared to a pilot plant, a commercial unit with four reactors in series is regenerated as follows. Naptha feed is withdrawn and hydrogen is circulated at high temperature to strip hydrocarbon from the catalyst. The separator and knockout drums are periodically drained of hydrocarbon. Hydrogen circulation is continued while the reactors are cooled to about 216°C (420°F). At 216°C (420°F), the recycle loop is purged with nitrogen and low points are checked for liquid hydrocarbons. After periodic draining shows that little or no hydrocarbon liquids are being collected, it is advantageous to switch to a fresh recycle gas dryer which is substantially free of hydrocarbons and water. If there is a recycle gas sulfur converter/sorber, it will be bypassed at this point.

When the reactor inlets are at 216°C (420°F) and the level of combustibles in the recycle gas is less than 2.0%, air is introduced to the recycle gas stream. The oxygen level at the first reactor inlet is adjusted to 0.5%. The burning of residual combustibles in the recycle gas consumes all the oxygen and results in a 44.4 to 69.4°C (80 to 125°F) exotherm across the first reactor. Eventually, the vapor-phase combustibles are consumed and the burn-wave moves through the reactor chain. After oxygen breakthrough occurs and the exotherm subsides, furnace temperatures are raised at rate of about 13.9°C/h (25°F/h) until peak catalyst bed temperature reaches 371°C (700°F). The total exotherm at this point is less than about 11.1°C (20°F). When oxygen conversion across the reactor train drops to less than 10%, the oxygen concentration at the reactor inlet is raised to 1.0 to 4.0% and the furnace temperatures are

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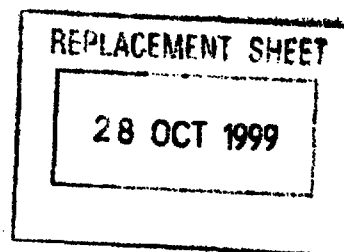
adjusted to maintain the peak catalyst bed temperatures as close to 371°C (700°F) as possible.

Temperatures are maintained at 371°C (700°F) for 12 to 24 hours before the air makeup is stopped. The recycle loop is then purged with nitrogen and cooled to 260°C (500°F). At 260°C (500°F) the recycle gas dryers are switched again and the sulfur converter/sorber is brought back on-line. About twice the stoichiometric amount of hydrogen needed for reduction of the catalyst is fed into the unit over a period of about an hour. The unit is then partially depressured and pressured up with hydrogen to adjust the hydrogen to nitrogen ratio to about one-to-four. Higher hydrogen to nitrogen ratios can result in excessive ammonia formation, which is catalyzed by the iron particles present in the reactor tubes. The temperature is held at 260°C (500°F) for about an hour then raised 5.6°C/h (10°F/h) to 430°C (900°F). The hydrogen/nitrogen ratio is maintained by adjusting hydrogen and nitrogen makeup rates. The temperature is held at 480°C (900°F) for at least 12 hours. When water in the fourth reactor effluent is less than 100 ppm, the temperature is dropped to 371°C (700°F) or lower to await feed introduction.

EXAMPLE XII (for comparison only)

Reforming With A Silicalite Catalyst/Catalyst Coking

A silicalite catalyst was produced by impregnating a dried synthesized Silicalite powder to give 1% Pt on the Silicalite powder, then mixing this with SAPO-11 powder to produce a finished catalyst consisting of 25% wt SAPO-11 and 75% wt Pt Silicalite.



This catalyst was used to convert hexane containing feeds to aromatics. The feed compositions are listed in Table 3. The conversion conditions used were a pressure of 303 kPa (30 psig), a WHSV of 0.72, a hydrogen to hydrocarbon ratio of seven to one, with the catalyst temperatures ranging from 470°C - 540°C (880 to 1000°F) to maintain a high product benzene level and adjust for fouling.

EXAMPLE XIII

Regeneration Of Silicalite Catalyst (for comparison only)

The catalyst of Example XII was repeatedly coked and regenerated. The regeneration conditions included treating the catalyst with low concentrations (0.5 to 2.0 wt. %) of oxygen at 303 to 786 kPa (30 to 100 psig) at a GHSV of 923. During regeneration, the regeneration gases contained less than 100 ppm water.

The regeneration temperature was varied over the range of 230 to 360°C (450 to 680°F). Regenerations below about 260°C (500°F) for 16 to 24 hours were not successful in producing a catalyst having an activity (as measured by hexane conversion) or a selectivity (as measured by the wt. % benzene in the product) similar to fresh catalyst. At regeneration temperatures between 290 and 360°C (550 and 680°F), aromatization activity was restored to about that of the start of the run cycle.

Table 2, below, shows the regeneration temperatures and times for several of these regenerations, along with the activity and selectivity results. The regenerated catalyst was able to maintain product benzene levels of about 40 wt. %, for greater than 1000 hours between regenerations.

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24TABLE 2
SELECTIVITY AND ACTIVITY RESULTS*

Regen. No.	Temp. °C (°F)	Hours	O ₂ Level %	Pressure kPa (psig) #	Before Regen.		After Regen.		Hours on Stream ^{1,2,4} Producing BZ
					Hexane Conv.	Product Wt. % BZ	Hexane Conv.	Product Wt. % BZ	
10	316 (600)	72.0	0.5	303 (30)	55	14	74	41	1200
	330 (630)	46.7	1.0	786 (100)					
11	316 (600)	46.8	1.0	786 (100)	82	27	68	39	1200
	330 (630)	3.6	1.0	786 (100)					
12	316 (600)	26.3	1.0	786 (100)	86	8	72	41	1700
	330 (630)	65.3	1.0	786 (100)					
	350 (660)	119.2	1.0	786 (100)					
13	316 (600)	66.6	1.0	786 (100)	59	24	98	39	1000+ ¹⁵
	330 (630)	24.9	1.0	786 (100)					
	350 (660)	30.9	1.0	786 (100)					
	360 (680)	4 ^{1/2} ₉	1.0	786 (100)					
0	Fresh Catalyst at 21 Hrs. on Stream				98 ¹⁶	42 ¹⁶			

*Conversion Conditions: 303 kPa (30 psig), WHSV = 0.72, Catalyst Temp. 471 °C to 540 °C (880 °F to 1000 °F)

¹Utilizing Feed B (Table 3)²At constant (40%) aromatization activity.³Utilizing Feed A (Table 3)⁴BZ = Benzene⁵Run was voluntarily terminated; catalyst remained active.

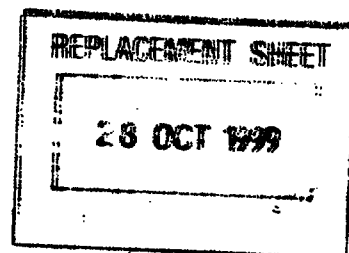


TABLE 3

FEED COMPOSITION

<u>COMPOUND</u>	FEED A	FEED B
	LIGHT NAPHTHA	MODEL FEED
	<u>wt. %</u>	<u>wt. %</u>
Total C ₃	16.1	0.0
Total C ₆	49.7	70.0
Total C ₇	34.2	24.0
N-C ₄	12.5	70.0
Methyl Cyclohexane	5.9	6.0

Feed A used for start of run.

Feed B used for regeneration studies.

EXAMPLE XIV

Effect of Raising Temperature After
Substantially Completing Carbon Burn at Low Temperatures

This example shows that temperature may be raised beyond the 416°C (780°F) limit after substantially completing a halogen-free carbon burn regeneration at lower temperatures. A platinum on barium exchanged L-zeolite catalyst was used to reform a light naphtha feedstock very similar to the one shown in Table 1 of the specification. At the end of the run, the catalyst was regenerated as follows.

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The naphtha feed was stopped. The reactor was cooled to 260°C (500°F) while adding makeup hydrogen. After reaching 260°C (500°F), the unit was purged with nitrogen gas to remove substantially all of the hydrogen. Any remaining liquid hydrocarbons were drained from the gas liquid separator and other low points in the system. The nitrogen makeup rate was then reduced to a low level, the sulfur converter/sorber was by-passed, and the pressure and recycle gas rate were adjusted to about 683 kPa (85 psig) and 100 GHSV, respectively.

After purging the recycle loop with nitrogen, air was added through a mass flowmeter to bring the reactor inlet oxygen concentration to 0.5%. After holding for two hours at 260°C (500°F), the temperature was raised 13.9°C/h (25°F/h) to 404°C (760°F) while the inlet oxygen level was maintained between 0.4 and 0.6%. The temperature was then held overnight at 404°C (760°F) with the inlet oxygen level between 1.0 and 1.3%.

After 16 hours at 404°C (760°F), the carbon burn was substantially complete as indicated by the difference between inlet and oxygen concentrations which was less than 0.05%. The temperature was then raised to 454°C (850°F) and maintained at 454°C (850°F) for 14 hours. A small amount of additional burning occurred at the high temperature but at a very low rate.

The reactor was then purged with nitrogen and a fresh recycle gas dryer brought on-line while the reactor cooled to 260°C (500°F). When the water level in the reactor effluent was less than 100 ppm, catalyst reduction was initiated by pressuring from 683 to 786 kPa (85 to 100 psig) with hydrogen. The nitrogen makeup gas was stopped and pressure was maintained at 786 kPa (100 psig) by adding hydrogen makeup gas. The temperature was held at 260°C (500°F) for two hours and then raised 5.6°C/h (10°F/h) to 480°C (900°F).

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Feed was reintroduced and the reforming reaction was resumed at the same conditions used in our previous examples and temperature was adjusted to maintain 42 wt. % aromatics in the liquid product. After 1070 hours on-stream, a least-squares plot was made of the data from 136 to 1070 hours. From this plot, it was determined that the start-of-run temperature was 464°C (868°F) and the fouling rate was 0.011°C/h (0.020°F/h), which compares to 454°C (850°F) and 0.014°C/h (0.026°F/h), respectively, for fresh catalyst. The projected run length was 3350 hours compared to 3300 for fresh catalyst. The regeneration was not as good as those of the previous examples where temperature was kept below 416°C (780°F) but was considered acceptable.

As can be seen by this Example, there was no improvement in catalyst performance obtained by raising temperature of the oxygen after substantially completing the carbon burn at a temperature below 416°C (780°F).

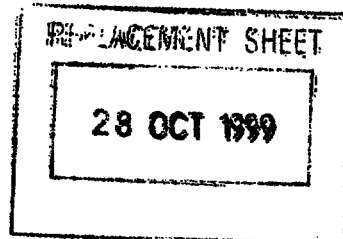
EXAMPLE XV

Regeneration with up to 520 ppm Water in the Recycle Gas

This experiment shows that up to 520 ppm water is present in the recycle gas and an acceptable regeneration is achieved.

Also, one may consider using a less expensive dessicant than molecular sieves in the recycle gas dryer, such as silica-gel or activated alumina.

The catalyst from Example II was regenerated a second time as follows. Preparations for the carbon burn were the same



as above. Before adding air, water was added to the recycle gas stream by bubbling makeup nitrogen through water contained in a small bomb. The makeup nitrogen feed rate was adjusted to obtain about 500 ppmv water in the gas stream entering the reactor and air was added to bring the oxygen level to 0.5%. During the carbon burn, the reactor inlet oxygen level was maintained between 0.4 and 0.6 and the inlet water level between 420 and 520 ppmv by adjusting the air and nitrogen feed rates.

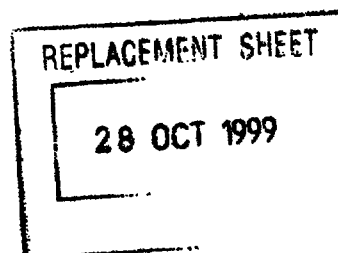
After holding for two hours at 260°C (500°F); the temperature was raised 13.9°C/h (25°F/h) to 371°C (700°F) while maintaining inlet oxygen levels between 0.4% and 0.7%. The temperature was then held 20 hours at 371°C (700°F) with the inlet oxygen level rising from 0.6 and 1.2%. The air was then shut off and dry makeup nitrogen was substituted for water-saturated nitrogen. A fresh dryer was put on-line and the reactor was cooled to 260°C (500°F).

When the water level in the reactor effluent was less than 100 ppm, the catalyst was reduced and the reforming reaction resumed as in the previous example. After 600 hours on-stream, the start-of-run temperature and fouling rate were calculated to be 468°C (875°F) and 0.010°C (0.0186°F) respectively. This corresponds to a projected run length of 3225 hours, which is close to that of fresh catalyst.



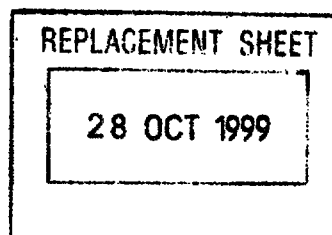
WHAT IS CLAIMED IS:

1. A process for regenerating a coke-contaminated reforming catalyst comprising platinum on a L-zeolite or silicalite molecular sieve, said process comprising of:
 - (a) contacting said catalyst in a catalyst zone with a halogen-free oxygen-containing gas at a temperature of less than 416°C (780°F), said gas having a water content of from 100 ppmv to 1000 ppmv; and
 - (b) oxidizing at least a portion of said coke to produce a combustion gas for a sufficient period of time such that the catalyst aromatization activity is restored to within 11.1°C (20°F) of the activity said catalyst possessed at the start of the previous run cycle.
2. A process according to claim 1, further comprising the steps of:





- (a) passing at least a portion of said combustion gas through a dryer to produce a dried gas having a water content less than said portion of combustion gas; and
 - (b) recycling at least a portion of said dried gas to said catalyst zone.
3. A process according to claim 2, further comprising the step of:
- (a) reducing the regenerated catalyst by contacting the catalyst with a gaseous stream containing





hydrogen at an initial temperature from 149°C to 371°C (300°F to 700°F).

4. The process as recited in Claim 1, 2 or 3 wherein the oxygen content of the oxygen containing gas is from between 0.1 to 21.0 mole % oxygen.
5. The process as recited in Claim 1, 2 or 3 wherein the oxygen content of the oxygen containing gas is from 0.2 to 4.0 mole %.
6. The process as recited in Claim 1, 2 or 3 wherein the L-zeolite further comprises an alkaline earth metal.
7. The process as recited in Claim 1, 2 or 3 wherein the L-zeolite further comprises boron.
8. The process as recited in Claim 1, 2 or 3 wherein said catalyst is bound with a support matrix comprising alumina, silica or mixtures thereof.

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9. The process as recited in Claim 3 further comprising raising the temperature of the gaseous stream containing hydrogen to between 427°C and 540°C (800°F and 1000°F) to complete the dryout and reduction.
10. The process as recited in Claim 3 wherein the carbon burn is initiated at a temperature of less than 260°C (500°F).
11. The process as recited in Claim 14 wherein the temperature is escalated during the carbon burn in a slow ramping fashion.
12. The process as recited in Claim 14 wherein the temperature is escalated during the carbon burn in a stepwise fashion.
13. The process as recited in Claim 1, 2 or 3 wherein the peak catalyst temperature during the carbon burn step is between 316°C and 400°C (600°F and 750°F).
14. The process as recited in Claim 3 wherein prior to reducing the catalyst, the catalyst is purged with an inert gaseous stream.
15. The process as recited in Claim 3 further comprising:
 - (a) passing at least a portion of said gaseous stream containing hydrogen through a dryer; and
 - (b) recycling a portion of said gaseous stream containing hydrogen to said catalyst zone.
16. The process as recited in Claim 3 further comprising reducing the regenerated catalyst by contacting the

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- catalyst with a gaseous stream containing a mixture of inert gas and hydrogen at a temperature between 480°C and 540°C (900°F and 1000°F).
17. The process as recited in Claim 3 further comprising reducing the regenerated catalyst by contacting the catalyst with a gaseous stream containing a mixture of nitrogen and hydrogen at a temperature between 480°C and 540°C (900°F and 1000°F).
 18. The process as recited in Claim 21 wherein the mole ratio of nitrogen gas to hydrogen gas is at least 4:1.
 19. The process as recited in Claim 3 further comprising the step of purging the catalyst resulting from step (b) with a gaseous stream comprising nitrogen prior to the reduction step (c).
 20. The process as recited in Claim 3 further comprising the step of purging the catalyst resulting from step (b) with a gaseous stream comprising nitrogen prior to the reduction step (c) and changing the recycle gas dryer so as to reduce carbon dioxide in the recycle gas to less than 100 ppm.
 21. The process as recited in Claim 3 wherein the L-zeolite catalyst contains barium.
 22. A reforming process wherein a reforming catalyst is regenerated for at least two cycles by the process as recited in Claim 1, 2 or 3.
 23. The process as recited in Claim 1, 2 or 3 wherein the catalyst is continuously withdrawn from reactors for regeneration in a separate vessel, and returned to the reactors.

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24. A reforming process comprising contacting a hydrocarbon feed with a platinum containing L-zeolite or silicalite molecular sieve catalyst under reforming conditions and regenerating said catalyst in accordance with the process of Claim 1, 2 or 3.

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LOW TEMPERATURE REGENERATION OF COKE DEACTIVATED
REFORMING CATALYSTS

ABSTRACT

A process for generating a coke contaminated reforming catalyst comprising platinum on a molecular sieve, said process consisting essentially of contacting said catalyst with a halogen-free oxygen-containing gas at a temperature of less than 780°F for a sufficient period of time such that the aromatization activity is restored to within 20°F of the activity said catalyst possessed at the start of the previous run cycle.

