

PROCESS FOR THE REGENERATION OF
HYDROCARBON CONVERSION CATALYSTS

Field of the Invention

5 The present invention relates to hydrocarbon conversion processes, especially a process for producing aromatic hydrocarbons from lower alkanes. More specifically, the invention relates to a process for increasing the productivity of a hydrocarbon conversion catalyst which is subject to coking, especially an aromatization catalyst used in a dehydroaromatization process.

Background of the Invention

15 Catalytic hydrocarbon conversion reactions such as naphtha reforming, hydrocracking, heavy oil pyrolysis, catalytic cracking, catalytic dewaxing, dehydrogenation, isomerization, alkylation, transalkylation, and dealkylation are well-known. After a period of time in use during the course of a hydrocarbon conversion reaction the catalyst may become deactivated as a result of mechanisms such as the deposition of coke on the catalyst particles. Coke is comprised primarily of carbon, but is also comprised of a small quantity of hydrogen. Coke decreases the ability of the catalyst to promote reactions to the point that continued use of the catalyst is no longer practical or economical. At that point, the catalyst must be discarded or more preferably, reconditioned, or regenerated, so it can be reused.

20 Numerous catalyst regeneration methods are described in the patent literature and nearly all involve to some extent the combustion of coke from the surface of the catalyst. The particular method of regeneration that a specific process employs depends on the design of the catalyst bed(s) in the reactor(s). Fixed catalyst beds keep the catalyst stationary. When the catalyst in a fixed bed reactor becomes

deactivated, the reactor is generally temporarily taken out of service while the catalyst is either regenerated in situ or else unloaded and replaced with regenerated or fresh catalyst. Two types of fixed bed regeneration methods are used commercially: cyclic regeneration and semi-regeneration. In the cyclic regeneration method, at least one or at most not all of the reactors are taken out of service at any one time and the process continues in operation with the remaining reactor(s). After the deactivated catalyst is regenerated, the reactor is placed back in service, which in turn allows another reactor to be taken out of service after regeneration of the catalyst.

Lower alkane aromatization is a highly endothermic reaction that is thermodynamically favored at high temperature and low pressure. Unfortunately, these conditions also facilitate formation of surface coke deposits that deactivate the catalyst relatively rapidly. The coke deposits may be partially or fully removed by subjecting the catalyst to a high-temperature stripping operation with hydrogen-containing gas or steam, or by using an oxygen-containing gas to burn off the accumulated coke. A coke burn is generally preferred for full removal of the accumulated coke deposits, but it must be conducted in a relatively slow, carefully controlled manner to avoid excessive temperature increases that may cause irreversible loss of active catalyst surface area. The useful life of the catalyst is adversely affected if the catalyst is subjected to a large number of high-temperature coke burns between exposures to the lower alkane feed and aromatization conditions. This also applies to catalysts used in other hydrocarbon conversion reactions.

It would be advantageous to provide a catalytic hydrocarbon conversion process wherein (a) the deactivation of the catalyst because of coke formation and (b) the adverse

effects of high-temperature coke burns can be minimized. It would also be advantageous to provide a regeneration process that can be integrated into a process for the conversion of hydrocarbons.

5 Summary of the Invention

The present invention provides a process for regeneration of a hydrocarbon conversion catalyst subject to coking which comprises:

- 10 (a) alternately contacting a hydrocarbon feed with a catalyst under conversion reaction conditions in a reactor for a short period of time, preferably about 30 minutes or less, to produce reaction products and then contacting the catalyst with hydrogen-containing gas at elevated temperature for a short period of time, preferably about 30 minutes or
15 less,
- (b) repeating the cycle of step (a) at least one time,
- (c) regenerating the catalyst by contacting it with an oxygen-containing gas at elevated temperature,
- (d) optionally subjecting the regenerated catalyst to a
20 metal redispersal treatment,
- (e) optionally reducing the regenerated catalyst, preferably a with hydrogen-containing gas,
- (f) optionally sulfiding the catalyst, and
- (g) repeating steps (a) through (f) at least one time.

25 Brief Description of the Drawings

Fig. 1 is a graph which compares the ethane conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 1 and 2 in Example 1.

Fig. 2 is a graph which compares the total (ethane +
30 propane) conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 3 and 4 in Example 2.

Fig. 3 is a graph which compares the ethane conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 5 and 6 in Example 3.

Fig. 4 is a graph which compares the ethane conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 5 and 7 in Example 3.

Detailed Description of the Invention

Hydrocarbon conversion reactions are catalytic processes in which hydrocarbon compounds are converted to different hydrocarbon compounds. Examples of suitable hydrocarbon conversion reactions for which the present invention may be utilized include naphtha reforming, hydrocracking, heavy oil pyrolysis, catalytic cracking, catalytic dewaxing, dehydrogenation, isomerization, alkylation, transalkylation, and dealkylation.

As described above, catalytic hydrocarbon conversion processes frequently have significant problems with a build-up of coke on the catalyst. This invention provides a unique process for regenerating coked catalysts. The regeneration process will be described below in connection the aromatization of lower alkanes but it may be used with other hydrocarbon conversion reactions as well.

In the preferred operation/regeneration scheme of the present invention, at any given time a majority of the parallel arranged fixed-bed reactors in a given set are subjected to alternating cycles of (a) short-time (preferably about 30 minutes or less, more preferably about 20 minutes or less, and most preferably about 10 minutes or less, but generally not less than 1 minute) exposure to the lower alkane feed at suitable lower alkane aromatization conditions and (b) short-time (preferably about 30 minutes or less, more preferably about 20 minutes or less, and most preferably about 10 minutes or less, but generally not less than 2

minutes) stripping with a hot hydrogen-containing gas to reheat the catalyst bed and reduce catalyst performance decline by partial removal of surface coke deposits. The timing of this cycling is such that at any given time at least one reactor in the set is exposed to feed and producing aromatics at all times and at least one reactor is exposed to stripping with a hot hydrogen-containing gas at all times. At the same time, at least one of the reactors in the set is completely offline for controlled coke burn regeneration and metal redispersal and/or reduction with a hydrogen-containing gas and/or sulfiding, if needed. Upon completion of the coke burn, the reactor is brought back online for reaction/stripping cycles while another of the parallel arranged reactors, with spent catalyst, is taken offline for coke burn. The pattern continues until all of the reactors have been subjected to coke burn and then repeats. In this way, continuous production of products at high yield is maintained, despite the inherently rapid coking/deactivation of the catalyst under the reaction conditions.

The operation/regeneration scheme described above enables continuous production of products from hydrocarbon feeds at commercially viable rates and yields. This scheme meets the need for frequent catalyst regeneration (coke removal) in a lower alkane aromatization process in a manner that extends the useful operating life of the catalyst or catalysts employed. The alternation of feed exposure and stripping with hot hydrogen-containing gas in the majority of the parallel reactors at any given time reduces catalyst performance decline over one operational cycle (time between coke burns). This reduction of catalyst performance decline extends the time before a slower, properly-controlled coke burn that will reduce irreversible damage to the catalyst becomes necessary. The useful life of the catalyst is

substantially longer when used according to the present invention than if the catalyst is subjected to a higher number of high-temperature coke burns between exposures to the feed and reaction conditions.

5 Stripping of coked catalysts with hot hydrogen-containing gas has been practiced commercially for decades and various methods are known to those skilled in the art. The stripping of the catalyst may be carried out in the reactor. The stripping may be carried out by exposing the
10 catalyst to a stream containing up to 100% hydrogen at from about 150 to about 800°C, from about 0.01 to about 15.0MPa and a weight hourly space velocity (WHSV) of from about 0.1 to about 10 hr⁻¹.

Regeneration of coked catalysts has also been practiced
15 commercially for decades and various regeneration methods are known to those skilled in the art. The regeneration of the catalyst may be carried out in the reactor. For example, the catalyst may be regenerated by burning the coke at high temperature in the presence of an oxygen-containing gas as
20 described in U.S. patent no. 4,795,845 which is herein incorporated by reference in its entirety. The preferred regeneration temperature range for the coke burn regeneration step herein is from about 200 to about 700°C, more preferably from about 300 to about 550°C. The coke burn regeneration
25 method preferred for use herein is to use air or nitrogen-diluted air at about 0.01 to about 1.0 MPa pressure and about 300 to about 2000 GHSV feed rate and at a starting temperature nearer to the lower end of the above preferred range which is increased continuously or stepwise to reach a
30 temperature nearer to the upper end of the above preferred range.

The optional metal redispersion step may be carried out by oxychlorination, or by treatment with a solution

containing one or more metal redispersing agents, or by various other means known in the art. Metal redispersion methods have been practiced commercially for decades and various methods are known to those skilled in the art.

- 5 Oxychlorination is preferred for many Pt-containing catalysts, including alumina-supported naphtha reforming catalysts. The steps involved in naphtha reforming catalyst regeneration, including oxychlorination, are described in a review article entitled, "Catalyst Regeneration and
- 10 Continuous Reforming Issues, by P. K. Doolin, D. J. Zalewski, and S. O. Oyekan, on pages 443-444 of the book Catalytic Naphtha Reforming, 2nd. Edition, edited by G. J. Antos and A. M. Aitani (published by Marcel Dekker, Inc., New York, 2004).

- Oxychlorination is preferably carried out with a gas
- 15 mixture containing water, oxygen, hydrogen chloride and chlorine, and/or one or more organochlorine compounds, such as perchloroethylene, capable of reaction to release chlorine under oxychlorination reaction conditions. Preferably, the oxychlorination step is conducted at a temperature ranging
- 20 from about 480 to about 520°C, with the total concentration of chlorine-containing species in the gas ranging from about 0.01 to 0.6 mol %, the oxygen content of the gas ranging from about 0.1 to about 20 mol % at a partial pressure of up to ca. 25 psia. However, it should be noted, and is well-
- 25 known to those skilled in the art, that variations in reactor equipment capabilities and metallurgy and/or safety concerns may require upper limits on chlorine compound and/or oxygen content that are substantially lower than those given here in some cases.

- 30 The optional reduction step, preferably carried out with hydrogen-containing gas, has been practiced commercially for decades and various methods are known to those skilled in the art including those that use other reducing gases such as

carbon monoxide. The reduction serves the purpose of reducing the catalyst metal component to the elemental metallic state and to ensure a relatively uniform dispersion of the metal throughout the support. It may be carried out

5 according to the process described in U.S. Patent No.

5,106,800, which is herein incorporated by reference in its entirety, specifically by exposing the catalyst to hydrogen-containing gas at a flow rate ranging from about 500 to 6000 GHSV, pressure ranging from about 0.05 to 15.0 MPa, and

10 temperature ranging from about 200 to about 800°C. Sulfiding is another catalyst treatment that has been used for many years in the reactivation of catalysts. It serves the purpose of moderating the catalyst activity to prevent excessive hydrogenolysis and coking reactions. It may be carried out

15 according to the process described in U.S. Patent No.

5,106,800, which is herein incorporated by reference in its entirety, specifically by treating the reduced catalyst with a sulfiding gas such as a mixture of hydrogen and hydrogen sulfide and/or one or more volatile organosulfur compounds
20 having at least about 10 moles of hydrogen per mole of hydrogen sulfide, more preferably at least 50 moles of hydrogen per mole of sulfur compound(s) at a temperature of from about 200 to about 700°C.

Suitable hydrocarbon feed streams for use herein include
25 streams which may contain alkanes, naphthenes, olefins, and/or aromatics. The feed may comprise a single hydrocarbon or mixtures of various hydrocarbons with carbon numbers ranging from 1 to 20 or more.

In one embodiment, the feed may be comprised of
30 primarily one or more C₂, C₃, and/or C₄ alkanes (referred to herein as "lower alkanes"), for example an ethane/propane/butane-rich stream derived from natural gas, refinery or petrochemical streams including waste streams.

Examples of potentially suitable feed streams include (but are not limited to) residual ethane and propane from natural gas (methane) purification, pure ethane, propane and butane streams (also known as Natural Gas Liquids) co-produced at a liquefied natural gas site, C₂-C₅ streams from associated gases co-produced with crude oil production, unreacted ethane "waste" streams from steam crackers, and the C₁-C₄ byproduct stream from naphtha reformers. The lower alkane feed may be deliberately diluted with relatively inert gases such as nitrogen and/or with various light hydrocarbons and/or with low levels of additives needed to improve catalyst performance.

The present invention includes a process for producing aromatic hydrocarbons which comprises bringing into contact a hydrocarbon feedstock containing lower alkanes, and possibly other hydrocarbons, and a catalyst composition suitable for promoting the reaction of such hydrocarbons to aromatic hydrocarbons, such as benzene, at a temperature from about 400 to about 700°C and a pressure from about 0.01 to about 1.0 Mpa absolute. The gas hourly space velocity (GHSV) per hour may range from about 300 to about 6000. The process may be carried out in a single stage or in multiple, preferably two, stages. If a two-stage process is used, the conditions in each stage may fall in the above ranges and may be the same or different. Preferred aromatization processes are described in U.S. Application No. 61/257085, filed November 2, 2009, entitled "Process for the Conversion of Mixed Lower Alkanes to Aromatic Hydrocarbons," and U.S. Application No. 61/257149, filed November 2, 2009, entitled "Process for the Conversion of Lower Alkanes to Aromatic Hydrocarbons," both of which are herein incorporated by reference in their entirety.

Catalysts which may be used in the aromatization process of the present invention are described in U.S. 7,186,871 and U.S. 7,186,872, both of which are herein incorporated by reference in their entirety. The first of these patents describes a platinum containing ZSM-5 crystalline zeolite synthesized by preparing the zeolite containing the aluminum and silicon in the framework, depositing platinum on the zeolite and calcining the zeolite. The second patent describes such a catalyst which contains gallium in the framework and is essentially aluminum-free. U.S. 5,227,557, hereby incorporated by reference in its entirety, describes catalysts which contain an MFI zeolite plus at least one noble metal from the platinum family and at least one additional metal chosen from the group consisting of tin, germanium, lead, and indium.

Preferred aromatization catalysts for use in this invention are described in U.S. Application No. 12/371787, filed February 16, 2009 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons," U.S. Provisional Application No. 61/029939, filed February 20, 2008 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons," and U.S. Application No. 12/371803, filed February 16, 2009 entitled "Process for the Conversion of Ethane to Aromatic Hydrocarbons." These applications are hereby incorporated by reference in their entirety. They describes catalysts comprising: (1) platinum, (2) an amount of an attenuating metal selected from the group consisting of gallium, iron, tin, lead, and germanium; (3) f an aluminosilicate, preferably a zeolite, preferably selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, or ZSM-35, preferably converted to the H⁺ form, preferably having a SiO₂/Al₂O₃ molar ratio of from 20:1 to 80:1, and (4)

a binder, preferably selected from silica, alumina and mixtures thereof.

EXAMPLES

5

The following examples are provided for illustrative purposes only and are not intended to limit the scope of the invention.

10 Example 1

This example illustrates one aspect of the lower alkane aromatization process operating/catalyst regeneration scheme of the present invention. Specifically, this example shows a reduction in catalyst performance decline and coke formation
15 obtainable by operating the process with rapid cycling between hydrocarbon feed exposure and hot hydrogen stripping steps, as opposed to continuous exposure to the hydrocarbon feed. The hydrocarbon feed used for aromatization in this example consists of 100% ethane.

20 Catalyst A was made on 1.6 mm diameter cylindrical extrudate particles containing 80%wt of zeolite ZSM-5 CBV 3014E powder (30:1 molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, available from Zeolyst International) and 20%wt gamma-alumina binder. The extrudate samples were calcined in air up to 650°C to remove
25 residual moisture prior to use in catalyst preparation. The target metal loadings for Catalyst A were 0.025%w Pt and 0.09%wt Ga.

30 Metals were deposited on 25-100 gram samples of the above ZSM-5/alumina extrudate by first combining appropriate amounts of stock aqueous solutions of tetraammine platinum nitrate and gallium(III) nitrate, diluting this mixture with deionized water to a volume just sufficient to fill the pores of the extrudate, and impregnating the extrudate with this solution at room temperature and atmospheric pressure.

Impregnated samples were aged at room temperature for 2-3 hours and then dried overnight at 100°C.

Samples of Catalyst A, prepared as described above, were tested "as is," without crushing, in Performance Tests 1 and 2. For each performance test, a 15-cc charge of fresh (not previously tested) catalyst was loaded into a quartz tube (1.40 cm inner diameter) and positioned in a three-zone furnace connected to an automated gas flow system.

Prior to each performance test, the catalyst charge was pretreated in situ at atmospheric pressure (approximately 0.1 MPa absolute) in the following manner:

(a) calcination with air at approximately 60 liters per hour (L/hr), during which the reactor wall temperature was raised from 25 to 510°C in 12 hours, held at 510°C for 4 hours, then further increased from 510°C to 621°C in 1 hour, then held at 621°C for 30 minutes;

(b) nitrogen purge at approximately 60 L/hr, 621°C, for 20 minutes; and

(c) reduction with hydrogen at 60 L/hr, 621°C, for 30 minutes.

For Performance Test 1, at the end of the above pretreatment, the hydrogen flow to the reactor was terminated and the catalyst charge was continuously exposed to 100% ethane feed at atmospheric pressure (ca. 0.1 MPa absolute), 621°C reactor wall temperature, and a feed rate of 1000 GHSV (1000 cc feed per cc of catalyst per hour), for a total of 13 hours.

To monitor changes in catalyst performance during the above test, the total reactor outlet stream was sampled and analyzed by an online gas chromatographic analyzer system. The first online sample was taken ten minutes after introduction of the ethane feed. Subsequent samples were taken every 70 minutes thereafter, for a total of 12 samples

during the test. Based on the composition data obtained from the gas chromatographic analysis, ethane conversion was calculated according to the following formula: % ethane conversion = 100 - %wt ethane in outlet stream. Yields per pass of benzene and total aromatics were given by the %wt amounts of benzene and total aromatics, respectively, in the reactor outlet stream.

At the end of this 13 hour test, the ethane flow to the reactor was terminated and hydrogen was re-introduced at a flow rate of 60 L/hr. The reactor furnace heaters were turned off and the catalyst was allowed to cool to ca. 38°C over a period of approximately 8 hours.

For Performance Test 2, at the end of the pretreatment described above the catalyst charge was subjected to 157 cycles of alternating exposure to ethane feed and hydrogen at atmospheric pressure (ca. 0.1 MPa) and 621°C reactor wall temperature according to the following protocol:

(a) 5 minutes of 100% ethane feed at 1000 GHSV

(b) 10 minutes of 100% hydrogen at 4000 GHSV.

The total cumulative exposure time of the catalyst to ethane feed under this test regime was 13.3 hours. The total runtime for the 157 ethane feed/hydrogen stripping cycles described above was 39.9 hours.

To monitor changes in catalyst performance during Performance Test 2, the total reactor outlet stream was sampled and analyzed near the end of selected 5 minute ethane exposure intervals by an online gas chromatographic analyzer system. Ethane conversion, benzene yield per pass, and total aromatics yield per pass were determined in the same manner as for Performance Test 1 above.

At the end of this test, the ethane flow to the reactor was terminated and hydrogen was re-introduced at a flow rate of 60 L/hr. The reactor furnace heaters were turned off and

the catalyst was allowed to cool to ca. 38°C over a period of approximately 8 hours.

The ethane conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 1 and 2 are compared in Figure 1. As shown in this figure, the losses in ethane conversion level, benzene yield and total aromatics yield exhibited by the catalyst were much greater during 13 hrs of continuous exposure to ethane feed (Performance Test 1) than during 13.3 hours of cumulative ethane feed exposure under the cyclic feed/hydrogen operating regime used in Performance Test 2. Consistent with these results, the coke (carbon) levels determined by ASTM Method D5291 on the spent catalyst samples from Performance Tests 1 and 2 were 12.2%wt and 7.6%wt, respectively.

Example 2

This example illustrates one aspect of the lower alkane aromatization process operating/catalyst regeneration scheme of the present invention. Specifically, this example shows a reduction in catalyst performance decline and coke formation obtainable by operating the process with rapid cycling between hydrocarbon feed exposure and hot hydrogen stripping steps, as opposed to continuous exposure to the hydrocarbon feed. The hydrocarbon feed used for aromatization in this example consists of 50%wt ethane and 50%wt propane.

Catalyst B was made on 1.6 mm diameter cylindrical extrudate particles containing 80%wt of zeolite ZSM-5 CBV 2314 powder (23:1 molar SiO₂/Al₂O₃ ratio, available from Zeolyst International) and 20%wt gamma-alumina binder. The extrudate samples were calcined in air up to 650°C to remove residual moisture prior to use in catalyst preparation. The target metal loadings for Catalyst B were 0.025%w Pt and 0.09%wt Ga.

Samples of Catalyst B, prepared as described above, were tested "as is," without crushing, in Performance Tests 3 and 4. For each performance test, a 15-cc charge of fresh (not previously tested) catalyst was loaded into a quartz tube (1.40 cm inner diameter) and positioned in a three-zone furnace connected to an automated gas flow system.

Prior to each performance test, the catalyst charge was pretreated in situ at atmospheric pressure (approximately 0.1 MPa absolute) in the following manner:

(a) calcination with air at approximately 60 liters per hour (L/hr), during which the reactor wall temperature was raised from 25 to 510°C in 12 hours, held at 510°C for 4 hours, then further increased from 510°C to 600°C in 1 hour, then held at 600°C for 30 minutes;

(b) nitrogen purge at approximately 60 L/hr, 600°C, for 20 minutes;

(c) reduction with hydrogen at 60 L/hr, 600°C, for 30 minutes.

For Performance Test 3, at the end of the above pretreatment, the hydrogen flow to the reactor was terminated and the catalyst charge was continuously exposed to a feed consisting of 50wt ethane plus 50wt propane at atmospheric pressure (ca. 0.1 MPa absolute), 600°C reactor wall temperature, and a feed rate of 1000 GHSV (1000 cc feed per cc of catalyst per hour), for a total of 26 hours.

To monitor changes in catalyst performance during the above test, the total reactor outlet stream was sampled and analyzed by an online gas chromatographic analyzer system. The first online sample was taken ten minutes after introduction of the ethane/propane feed. Subsequent samples were taken at selected intervals thereafter for the remainder of the test.

Based on the reactor outlet composition data obtained from the gas chromatographic analysis, hydrocarbon feed conversion levels were calculated according to the following formulas:

5 Ethane conversion, % = $100 \times (\% \text{wt ethane in feed} - \% \text{wt ethane in outlet stream}) / (\% \text{wt ethane in feed})$

Propane conversion, % = $100 \times (\% \text{wt propane in feed} - \% \text{wt propane in outlet stream}) / (\% \text{wt propane in feed})$

10 Total ethane + propane conversion = $((\% \text{wt ethane in feed} \times \% \text{ ethane conversion}) + (\% \text{wt propane in feed} \times \% \text{ propane conversion})) / 100$

At the end of this test, the ethane/propane feed flow to the reactor was terminated and hydrogen was re-introduced at a flow rate of 60 L/hr. The reactor furnace heaters were
15 turned off and the catalyst was allowed to cool to ca. 38°C over a period of approximately 8 hours.

For Performance Test 4, at the end of the pretreatment described above, the catalyst charge was subjected to 155 cycles of alternating exposure to 50/50 (w/w) ethane/propane
20 feed and hydrogen at atmospheric pressure (ca. 0.1 MPa) and 600°C reactor wall temperature according to the following protocol:

(a) 10 minutes of ethane/propane feed at 1000 GHSV

(b) 20 minutes of 100% hydrogen at 4000 GHSV.

25 The total cumulative exposure time of the catalyst to ethane feed under this test regime was 26 hours. The total runtime for the 155 cycles of ethane/propane feed exposure and hydrogen stripping described above was 78 hours.

To monitor changes in catalyst performance during
30 Performance Test 4, the total reactor outlet stream was sampled and analyzed near the end of selected 5 minute ethane exposure cycles by an online gas chromatographic analyzer system. Ethane conversion, propane conversion, total

hydrocarbon feed conversion, benzene yield per pass, and total aromatics yield per pass were determined in the same manner as for Performance Test 3 above.

At the end of this test, the ethane/propane feed flow to the reactor was terminated and hydrogen was re-introduced at a flow rate of 60 L/hr. The reactor furnace heaters were turned off and the catalyst was allowed to cool to ca. 38°C over a period of approximately 8 hours.

The total feed conversion, benzene yield, and total aromatics yield data obtained in Performance Tests 3 and 4 are compared in Figure 2. As shown in this figure, the losses in feed conversion level, benzene yield, and total aromatics yield exhibited by the catalyst were much greater during 26 hours of continuous exposure to the hydrocarbon feed (Performance Test 3) than during 26 hours of cumulative hydrocarbon feed exposure under the cyclic feed/hydrogen operating regime used in Performance Test 4. Consistent with these results, the coke (carbon) levels determined by ASTM Method D5291 on the spent catalyst samples from Performance Tests 3 and 4 were 13.9%wt and 8.3%wt, respectively.

Example 3

In this example, a single catalyst charge is taken through successive tests involving a hydrocarbon feed exposure/hydrogen stripping regime (as described in Examples 1 and 2) and catalyst regeneration procedures involving coke burnoff alone or coke burnoff followed by an oxychlorination treatment. This example illustrates possible operational sequences that could be employed in a single lower alkane aromatization reactor in the process of the present invention. The hydrocarbon feed used for aromatization in this example was 100% ethane.

In Performance Test 5, a fresh 15-cc charge of Catalyst A (see Example 1) was tested with rapid cycling between 100% ethane feed and hydrogen stripping under the same conditions and in the same manner as Performance Test 2 described above in Example 1. Total cumulative exposure time to ethane feed was 13.3 hours and the total runtime was 39.9 hours. At the end of this test, the ethane flow to the reactor was terminated, hydrogen was re-introduced at a flow rate of 60 L/hr, and the reactor wall temperature was lowered from 621°C to ca. 204°C in 5 hours. The reactor was then purged with nitrogen at atmospheric pressure (ca. 0.1 MPa) at a flow rate of 60 L/hr for 20 minutes, in preparation for a coke burnoff operation using air.

After the nitrogen purge step, the reactor feed was changed to 10 L/hr air at atmospheric pressure. The reactor wall temperature was then raised from ca. 204°C to 427°C in 5 hours, held at 427°C for 1.5 hours, raised from 427°C to 482°C in 1 hour, held at 482°C for 1.5 hours, raised from 482°C to 510°C in 1 hour, held at 510°C for 4 hours, and then the reactor was allowed to cool to ambient temperature.

Performance Test 6 was conducted in the same manner as Performance Test 5, using the spent, coke-burned charge of Catalyst A from Performance Test 5. At the conclusion of Performance Test 6, the catalyst charge was subjected to a second coke burnoff in air according to the same procedure as that employed at the end of Performance Test 5.

After this second coke burnoff, the spent Catalyst A charge was subjected to an oxychlorination treatment. For this treatment, the 15-cc charge of spent catalyst was loaded into a quartz tube (1.40 cm inner diameter) and positioned in a three-zone furnace and connected to a gas flow system. Nitrogen flow of 30 L/hr was established at atmospheric pressure (ca. 0.1 MPa) and the catalyst was heated from room

temperature to 500°C in 2 hours. When the 500°C temperature was reached, the gas flowing through the catalyst bed at atmospheric pressure was switched from 30 L/hr nitrogen to 30 L/hr of a gas mixture with the following compositional range:

5 ca. 1.8-2.0%mol oxygen, ca. 1.8-2.0%mol water, ca. 0.8-1.0%mol hydrogen chloride, ca. 0.2-0.3%mol chlorine, balance nitrogen. After 3 hours of exposure to this flowing gas mixture, the gas flowing over the catalyst was switched to 30 L/hr of a mixture consisting of ca. 1.8-2.0%mol oxygen, 1.8-

10 2.0%mol water, balance nitrogen, for 3 hours. At the end of this 3 hour period, the gas flowing over the catalyst was switched to 30 L/hr or air at atmospheric pressure and the catalyst bed was cooled to ambient temperature.

Performance Test 7 was conducted in the same manner as

15 Performance Test 5, using the 15-cc charge of Catalyst A that had been subjected to the oxychlorination treatment described above.

The ethane conversion, total aromatics yield and benzene yield data obtained in Performance Tests 5 and 6 are compared

20 in Figure 3. The average ethane conversion and total aromatics yield levels displayed by the regenerated catalyst in Performance Test 6 were about 93% of the corresponding values for the fresh catalyst charge in Performance Test 5. The average benzene yield level displayed by the regenerated

25 catalyst in Performance Test 6 was about 97% of the corresponding value for the fresh catalyst in Performance Test 5.

The ethane conversion, total aromatics yield and benzene yield data obtained in Performance Tests 5 and 7 are compared

30 in Figure 4. The average ethane conversion level displayed by the regenerated catalyst in Performance Test 7 was about 95% of the corresponding value for the fresh catalyst charge in Performance Test 5. The average total aromatics and

benzene yields given by the regenerated catalyst in Performance Test 7 were about 97 and 100%, respectively, of the corresponding values for the fresh catalyst in Performance Test 5.

5

Example 4

Based on the data from Examples 1 and 3 above, this example outlines a possible scheme for operation of a lower alkane aromatization process using multiple parallel fixed-bed reactors according to the present invention.

The hydrocarbon feed used for aromatization in this example is 100% ethane. In this example, five parallel fixed-bed reactors are operated in cycles lasting approximately 60 hours each. During each 60 hour cycle, each individual reactor operates in the following two modes:

- (a) ca. 36 hours in "feed/H₂" mode, in which the catalyst is subjected to rapid cycles of hydrocarbon feed (ca. 5 min) and hydrogen (ca. 10 min) as described for Performance Test 2 (see Example 1);
- (b) ca. 24 hours in "regen" mode, in which the catalyst undergoes coke burnoff (such as that described in Example 3), an optional oxychlorination or other metal redispersal step (such as that described in Example 3), and (if needed) a short reduction step with hydrogen in preparation for being brought back online in "feed/H₂" mode.

The timing of each individual reactor's 60 hour operational cycle is staggered so that, during any 12 hour period in the overall 60 hour cycle, three of the five parallel reactors are in "feed/H₂" operational mode, while the other two reactors are in "regen" mode. This staggered timing scheme for a five-reactor system is shown in Table 1 below.

During each 12 hour period in the overall 60 hour cycle, the timing of the feed exposure and hydrogen stripping steps in each of the three online (non-regenerating) reactors is staggered so that during any 15 minute period in the 12 hour interval, one reactor is on hydrocarbon feed producing benzene and other aromatics while the other two reactors are subjected to the hydrogen stripping treatment. This staggered timing scheme for the three parallel online reactors during each 15 minute interval is shown in Table 2.

With the staggered cyclic operating scheme summarized in Tables 1 and 2, aromatics production from a lower alkane feed can occur continuously over a fresh or recently-regenerated catalyst while still meeting the need for frequent catalyst regeneration to maintain overall performance.

Example 5

Based on the data from Examples 2 and 3 above, this example outlines a possible scheme for operation of a lower alkane aromatization process using multiple parallel fixed-bed reactors according to the present invention.

The hydrocarbon feed used for aromatization in this example consists of 50%wt ethane and 50%wt propane. In this example, four parallel fixed-bed reactors are operated in cycles lasting approximately 96 hours (4 days) each. During each 4 day cycle, each individual reactor operates in the following two modes:

(a) ca. 3 days (72 hours) in "feed/H₂" mode, in which the catalyst is subjected to rapid cycles of hydrocarbon feed (ca. 10 min) and hydrogen (ca. 20 min) as described for Performance Test 4 (see Example 2);

(b) ca. 1 day (24 hours) in "regen" mode, in which the catalyst undergoes coke burnoff (such as that described in Example 3), an optional oxychlorination or other metal

redispersal step (such as that described in Example 3), and (if needed) a short reduction step with hydrogen in preparation for being brought back online in "feed/H₂" mode.

The timing of each individual reactor's 4 day operational cycle is staggered so that, during any 1 day period in the overall 4 day cycle, three of the four parallel reactors are in "feed/H₂" operational mode, while the other reactor is in "regen" mode. This staggered timing scheme for a four-reactor system is shown in Table 3.

During each 24 hour period in the overall 96 hr cycle, the timing of the feed exposure and hydrogen stripping steps in each of the three online (non-regenerating) reactors is staggered so that, during any 30 minute period in the 24 hour interval, one reactor is on hydrocarbon feed producing benzene and other aromatics, while the other two reactors are subjected to the hydrogen stripping treatment. This staggered timing scheme for the three parallel online reactors during each 30 minute interval is shown in Table 4.

With the staggered cyclic operating scheme summarized in Tables 3 and 4, aromatics production from a mixed lower alkane feed can occur continuously over a fresh or recently-regenerated catalyst while still meeting the need for frequent catalyst regeneration to maintain overall performance.

TABLE 1

TIME IN 60-HR CYCLE	0-12 HRS	12-24 HRS	24-36 HRS	36-48 HRS	48-60 HRS
REACTOR 1 MODE	FEED/H ₂	FEED/H ₂	FEED/H ₂	REGEN	REGEN
REACTOR 2 MODE	REGEN	FEED/H ₂	FEED/H ₂	FEED/H ₂	REGEN
REACTOR 3 MODE	REGEN	REGEN	FEED/H ₂	FEED/H ₂	FEED/H ₂
REACTOR 4 MODE	FEED/H ₂	REGEN	REGEN	FEED/H ₂	FEED/H ₂
REACTOR 5 MODE	FEED/H ₂	FEED/H ₂	REGEN	REGEN	FEED/H ₂

5

TABLE 2

TIME IN 15-MIN FEED/H ₂ CYCLE	0-5 MIN	5-10 MIN	10-15 MIN
REACTOR 1 MODE	FEED	H ₂	H ₂
REACTOR 2 MODE	H ₂	FEED	H ₂
REACTOR 3 MODE	H ₂	H ₂	FEED

10

TABLE 3

TIME IN 96-HR CYCLE	0-24 HRS	24-48 HRS	48-72 HRS	72-96 HRS
REACTOR 1 MODE	FEED/H ₂	FEED/H ₂	FEED/H ₂	REGEN
REACTOR 2 MODE	FEED/H ₂	FEED/H ₂	REGEN	FEED/H ₂
REACTOR 3 MODE	FEED/H ₂	REGEN	FEED/H ₂	FEED/H ₂
REACTOR 4 MODE	REGEN	FEED/H ₂	FEED/H ₂	FEED/H ₂

15

TABLE 4

TIME IN 30-MIN FEED/H ₂ CYCLE	0-10 MIN	10-20 MIN	20-30 MIN
REACTOR 1 MODE	FEED	H ₂	H ₂
REACTOR 2 MODE	H ₂	FEED	H ₂
REACTOR 3 MODE	H ₂	H ₂	FEED

20

C L A I M S

1. A process for regeneration of a hydrocarbon conversion catalyst subject to coking which comprises:

- 5 (a) alternately contacting a hydrocarbon feed with an catalyst under conversion reaction conditions in a reactor for a short period of time, preferably 30 minutes or less, more preferably 20 minutes or less, most preferably 10 minutes or less, to produce reaction products and then
- 10 contacting the catalyst with hydrogen-containing gas at elevated temperature for a short period of time, preferably 30 minutes or less, more preferably 20 minutes or less, most preferably 10 minutes or less,
- (b) repeating the cycle of step (a) at least one time,
- 15 (c) regenerating the catalyst by contacting it with an oxygen-containing gas at elevated temperature,
- (d) optionally subjecting the regenerated catalyst to a metal redispersal treatment,
- (e) optionally reducing the regenerated catalyst,
- 20 preferably with hydrogen-containing gas,
- (f) optionally sulfiding the catalyst, and
- (g) repeating steps (a) through (f) at least one time.

2. The process of claim 1 wherein the process is carried
- 25 out in at least three reactors arranged in parallel and at least one reactor is operated according to step (c) and at least two reactors are operated according to step (a) and in at least one of the at least two reactors operated according to step (a) the catalyst is contacted with the hydrocarbon
- 30 feed and in at least one of the at least two reactors operated according to step (a) the catalyst is contacted with hydrogen-containing gas.

3. The process of claims 1 and 2 wherein the process is carried out in at least four reactors arranged in parallel and at least one reactor is operated according to step (c) and at least three reactors are operated according to step
5 (a) and in at least one of the at least three reactors operated according to step (a) the catalyst is contacted with the hydrocarbon feed and in at least one of the at least three reactors operated according to step (a) the catalyst is contacted with hydrogen-containing gas.

10

4. The process of claims 1 to 3 wherein step (a) is carried out at 400 to 700°C, 0.01 to 1.0 MPa and a gas hourly space velocity of 300 to 6000 hr⁻¹.

15 5. The process of claims 1 to 4 wherein step (c) is carried out at 400 to 700°C, preferably 400 to 550°C.

6. The process of claims 1 to 5 wherein the oxygen-containing gas in step (c) is air.

20

7. The process of claims 1 to 6 wherein, after step (c), the regenerated catalyst is subjected to metal redispersion, preferably by oxychlorination.

25 8. The process of claims 1 to 7 wherein, after step (e), the regenerated catalyst is sulfided.

9. The process of claims 1 to 8 wherein after step (d) the regenerated catalyst is reduced.

30