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(54) Title: PROCESS FOR PRODUCING MONOAROMATICS

(57) Abstract: The invention relates to a process for producing monoaromatics from a hydrocarbon feed comprising polyaromatics and monoaromatics, comprising a) contacting the hydrocarbon feed in the presence of hydrogen with a hydrotreatment catalyst for reducing sulfur and nitrogen components and saturating at least one of the aromatic rings of the polyaromatics in the hydrocarbon feed to obtain partially dehydrogenated polyaromatics, b) contacting the effluent obtained by step a) with a selective dehydrogenation catalyst for selectively dehydrogenating single ring naphthenic species in the effluent obtained by step a), wherein the dehydrogenation catalyst comprises an aluminosilicate or a silicate material having a mordenite framework inverted (MFI) structure wherein one or more transition metals are selectively deposited inside pore structure of the MFI structure and c) contacting the effluent obtained by step b) in the presence of hydrogen with a ring opening catalyst for opening saturated aromatic rings of the partially dehydrogenated polyaromatics in the effluent obtained by step b).

PROCESS FOR PRODUCING MONOAROMATICS

The present invention relates to a process for producing monoaromatics such as BTX from a hydrocarbon feed comprising polyaromatics.

Methods are known for producing valuable products such as BTX and LPG from hydrocarbon feeds such as heavy cycle oil, light cycle oil, carbon black oil, cracked distillate and pyoil. Such hydrocarbon feeds comprise a large amount of polyaromatics and require selective aromatic ring opening (ring cleavage) for obtaining desired products. Further, the amounts of sulfur and nitrogen impurities occurring therein are usually high. For reducing the amounts of sulfur and nitrogen impurities, the feeds in an aromatic ring opening reactor undergo a hydrotreatment step prior to the aromatic ring opening.

The hydrotreatment step removes sulfur and nitrogen species by the use of an array of hydrotreating catalysts containing hydrogenation functionalities. Simultaneously with the removal of sulfur and nitrogen, full or partial hydrogenation occurs. Typically, olefinic species are fully hydrogenated while polyaromatics are partially or fully hydrogenated and monoaromatic species are hydrogenated to single ring naphthenics.

Such process is known from US20070062848, which discloses a process for hydrocracking a feed comprising aromatic compounds containing at least two fused aromatic rings to produce a product stream comprising a mixture of C2-4 alkanes. The process comprises passing the feed stream to a ring saturation unit over an aromatic hydrogenation catalyst; passing the resulting stream to a ring cleavage unit; and separating the resulting product into a C2-4 alkanes stream, a liquid paraffinic stream and an aromatic stream.

Given the nature of selective ring opening (ring cleavage) processes, the partial hydrogenation of polyaromatics in the hydrotreating step is beneficial in promoting the ring cleavage. In contrast, the hydrogenation of monoaromatics which occur during the hydrogenation step reduces the amount of the monoaromatics obtained in the final effluent.

US8962900 discloses a method of producing aromatics and light paraffins, comprising: (a) introducing oils derived from oil, coal or wood into a hydrogenation and

reaction area, so that polycyclic aromatic components are partially saturated and cracked; (b) separating components obtained in (a) into hydrocarbonaceous components having 11 or more carbons, hydrocarbonaceous components having 6-10 carbons, and hydrocarbonaceous components having 5 or fewer carbons; and (c) recirculating the hydrocarbonaceous components having 11 or more carbons separated in (b) to (a), feeding the hydrocarbonaceous components having 6-10 carbons to an aromatic separation process and a transalkylation process so that at least a portion of aromatics is recovered, and feeding the hydrocarbonaceous components having 5 or fewer carbons to a light separation process thus obtaining paraffins.

It is an objective of the present invention to provide a process for obtaining monoaromatics with a high yield from a mixture comprising polyaromatics.

Accordingly, the present invention provides a process for producing monoaromatics from a hydrocarbon feed comprising polyaromatics and monoaromatics, comprising

a) contacting the hydrocarbon feed in the presence of hydrogen with a hydrotreatment catalyst for reducing sulfur and nitrogen components and saturating at least one of the aromatic rings of the polyaromatics in the hydrocarbon feed to obtain partially dehydrogenated polyaromatics,

b) contacting the effluent obtained by step a) with a selective dehydrogenation catalyst for selectively dehydrogenating single ring naphthenic species in the effluent obtained by step a), wherein the dehydrogenation catalyst comprises an aluminosilicate or a silicate material having a mordenite framework inverted (MFI) structure wherein one or more transition metals are deposited selectively deposited inside pore structure of the MFI structure and

c) contacting the effluent obtained by step b) in the presence of hydrogen with a ring opening catalyst for opening saturated aromatic rings of the partially dehydrogenated polyaromatics in the effluent obtained by step b).

As used herein, the term ‘polyaromatics’ is understood to mean aromatic compounds containing at least two fused aromatic rings, which may be unsubstituted or substituted.

As used herein, the term ‘monoaromatics’ is understood to mean aromatic compounds containing one aromatic ring, which may be unsubstituted or substituted.

As used herein, the term “partially dehydrogenated polyaromatics” is herein understood to mean compounds derived from polyaromatics wherein at least one of the aromatic rings of the polyaromatics is saturated. At least one aromatic ring is present in the partially dehydrogenated polyaromatics. Thus, it will be appreciated that the term “partially dehydrogenated polyaromatics” means compounds derived from polyaromatics wherein at least one of the aromatic rings of the polyaromatics is saturated (hydrogenated) and the rest of the aromatic rings is still not saturated (dehydrogenated).

As used herein, the term “selectively deposited on the inside pore structure of the MFI structure” is herein understood to mean that the transition metal(s) deposited on the aluminosilicate or silicate material are unevenly distributed so that a higher proportion of the deposited transition metal(s) is present in the pores versus the surface when compared to an aluminosilicate or silicate material on which the deposited transition metal(s) are evenly distributed.

In step a) of the process of the invention, at least part of the polyaromatics undergoes a reaction in which at least one of their aromatic rings is saturated (hydrogenated) to form partially dehydrogenated polyaromatics. At least part of the monoaromatics undergoes a reaction in which its aromatic ring is hydrogenated to form single ring naphthenic species.

In step b) of the process of the invention, the single ring naphthenic species are converted to monoaromatics. The dehydrogenation catalyst is arranged such that single ring naphthenic species can preferentially contact the transition metal and be dehydrogenated. This is achieved by the transition metal(s) deposited on the aluminosilicate or silicate material being unevenly distributed so that a higher proportion of the deposited transition metal(s) is present in the pores versus the surface. Since the transition metal is present selectively inside the pore structure of the MFI structure, the species which are dehydrogenated are primarily only the species which can enter inside the pore structure. Due to the dimensions of the pore structure, single ring naphthenic species can enter inside the pore structure of the MFI structure and contact with the transition metal to be dehydrogenated. In contrast, the partially dehydrogenated polyaromatics generated in step a) do not enter inside the pore structure of the MFI structure, so that they are not dehydrogenated back to polyaromatics. Hence, the effluent obtained by step b) comprises an increased amount

of monoaromatics and a decreased amount of single ring naphthenics compared to the effluent obtained by step a). The amounts of the other components such as the partially dehydrogenated polyaromatics are not substantially changed.

In step c) of the process of the invention, the saturated aromatic rings of the partially dehydrogenated polyaromatics are opened to form aromatics with one less ring.

According to the process of the invention, due to the increased amount of the monoaromatics in the stream obtained by step b), the final amount of the monoaromatics in the stream obtained by step c) is advantageously increased compared to a process in which step b) is not present.

hydrocarbon feed

The aromatic compounds of the polyaromatics and monoaromatics may be unsubstituted or partly or fully substituted, typically by substituents selected from the group consisting of C1-4, preferably C1-2 alkyl radicals. Non-substituted polyaromatics containing two fused aromatic rings is naphthalene and non-substituted polyaromatics containing three fused aromatic rings are anthracene and phenantrene. Non-substituted monoaromatics is benzene.

Preferably, the hydrocarbon feed used in the process of the present invention comprises at least 10 wt-% polyaromatics, more preferably at least 20 wt-% polyaromatics and most preferably at least 30 wt-% polyaromatics, for example 30-75 wt% polyaromatics. Preferably, the hydrocarbon feed is selected from the group consisting of heavy cycle oil, light cycle oil, carbon black oil, cracked distillate and pyoil.

The hydrocarbon feed may contain from 10 to 40 wt%, for example from 20-30 wt% of monoaromatics.

The hydrocarbon feed may contain sulphur and nitrogen in small amounts. Typically nitrogen may be present in the hydrocarbon feed in an amount less than 700 ppm, preferably from about 250 to 500 ppm. Sulphur may be present in the feed in an amount from 2000 to 7500 ppm, preferably from about 2,000 to 5,000 ppm. Prior to treatment in accordance with the process of the present invention the hydrocarbon feed may be treated to remove sulphur and nitrogen or bring the levels down to conventional levels for subsequent treatment of a feedstock.

step a)

In step a), the feed mixture is subjected to a hydrotreatment. This may be performed in known manner, such as described in US20070062848.

Generally the step is conducted at a temperature from 300 °C to 500 °C, preferably from 350 °C to 450 °C and a pressure from 2 to 10, preferably from 4 to 8 MPa.

The hydrogenation is carried out in the presence of a hydrogenation/hydrotreating catalyst on a refractory support. Hydrogenation/hydrotreating catalysts are well known in the art. Generally the catalysts comprise a mixture of nickel, tungsten (wolfram) and molybdenum on a refractory support, typically alumina. The metals may be present in an amount from 0.0001 to 5, preferably from 0.05 to 3, most preferably from 1 to 3 weight % of one or more metals selected from the group consisting of Ni, W, and Mo based on the total weight of the catalyst (e.g. support and metal). One, and typically the most common, active form of the catalyst is the sulphide form so catalyst may typically be deposited as sulphides on the support. The sulphidizing step could be carried out ex-situ of the reactor or in-situ before the hydrotreating reaction starts. Suitable catalysts include Ni, Mo and Ni, Co and Mo, W bimetallic catalysts in the above ranges.

The hydrogenation/hydrotreating catalyst also reduces the sulphur and nitrogen components (or permits their removal to low levels in the feed which will be passed to the cleavage process). Generally the hydrogenation/hydrotreating feed may contain from about 2000 to 7500 ppm of sulphur and from about 200 to 650 ppm of nitrogen. The stream leaving the hydrogenation/hydrotreating treatment should contain not more than about 100 ppm of sulphur and not more than about 20 ppm of nitrogen.

In this step, hydrogen is typically fed to the reactor to provide from 100 to 300, preferably from 100 to 200 kg of hydrogen per 1,000 kg of the feed mixture.

In this step, at least part of the polyaromatics undergoes a reaction in which at least one of their aromatic rings is saturated (hydrogenated) and partially dehydrogenated polyaromatics are formed. Typically, at least 60, preferably at least 75, more preferably at least 85 wt% of the polyaromatics have one aromatic ring fully saturated. Generally, a lower temperature and/or a higher pressure lead to a higher amount of the

polyaromatics having one aromatic ring fully saturated.

At least part of the monoaromatics undergoes a reaction in which its aromatic ring is hydrogenated to form single ring naphthenic species. The monoaromatics are less likely to be saturated than the polyaromatics. Typically, 10-50 wt% of the monoaromatics have its aromatic ring fully saturated.

In this step, when present, at least part of the olefinic species is saturated into paraffinic species. Typically, olefinic species undergo a full saturation.

step b)

Step b) involves subjecting the effluent obtained by step a) to a selective dehydrogenation in which the single ring naphthenic species are dehydrogenated to monoaromatics. This is done by contacting the effluent obtained by step a) with a dehydrogenation catalyst comprising an aluminosilicate or a silicate material having a mordenite framework inverted (MFI) structure wherein one or more transition metals are selectively deposited inside pore structure of the MFI structure.

Known means and methods which result in a transition metal being unevenly distributed over the pores and the surface of the aluminosilicate or silicate having MFI structure include ion exchange with a metal salt solution, wherein the transition metal ions are in excess of the acid sites comprised in the aluminosilicate or silicate material and wherein the transition metal ions can freely diffuse into the aluminosilicate or silicate material. The aluminosilicate or silicate material should be depleted of external acidity before the ion-exchange.

Known means and methods which result in a transition metal being selectively deposited inside the pore structure of the aluminosilicate or silicate having MFI structure include ion-exchange in the presence of an acid. For instance, the deposition of Pt using H_2PtCl_6 in the presence of HCl, oxalic acid or citric acid induces competitive adsorption effects that favor the deposition of Pt in the inner regions of the catalyst. If H_2PtCl_6 is dosed with an excess of HCl, oxalic acid or citric acid to a zeolite with a reduced acidity (and hence reduced external acidity) the Pt is selectively deposited inside the pore structure of the MFI structure. This is further explained in Catalysis: An Integrated Approach, 2nd Edition by van Santen et.al.,ISBN 9780444829634, p.468-469.

Known means and methods for determining the distribution of a transition metal inside the pore structure and on the surface of the aluminosilicate or silicate having MFI structure include SEM-EDX and HR-TEM.7.

Preferably, the transition metal is selected from group 9 and 10, preferably 10, preferably Pt.

Preferably, the amount of the transition metal is 0.05-3 wt%, more preferably 0.1-2 wt%, with respect to the total catalyst.

The dehydrogenation catalyst as used in step b) may comprise further components such as a binder. Known binders include, but are not limited to silica, alumina and clay, such as kaolin. Alumina (Al_2O_3) is the preferred binder. The dehydrogenation catalyst preferably comprises at least 10 wt%, most preferably at least 20 wt% binder and preferably comprises up to 40 wt% binder. The catalyst is preferably formed into shaped catalyst particles by any known technique, for instance by extrusion.

The MFI structure is characterized by a tridimensional pre system composed of interconnected 10-membered ring straight (e.g. 5.5 x 5.1 angstrom) and sinusoidal (e.g. 5.6 x 5.3 angstrom) channels.

In some preferred embodiments, the material having the MFI structure is a silicalite. Silicalites are known e.g. from US4061724, incorporated herein by reference in its entirety for all purposes. Silicalites are also later described in the article presented in Nature, Vol. 271, Silicalite, A New Hydrophobic Crystalline Silica Molecular Sieve, E. M. Flanigen, et al., (February 1978), pp. 512-516, which is herein incorporated by reference for all purposes. As used herein, the term “silicalite” is meant to refer to those compositions described in US4061724. Such silicalites are formed from precursors of silica materials that contain little or no alumina (Al2O3). The inclusion of such alumina materials is considered to be an impurity in such silicalite precursors. Because commercially available silica sources typically are not completely free from such alumina compounds, there may be some amount of alumina in the silicalite as an impurity. For example, commercial silica sols may contain from about 500 to 700 ppm aluminum, while fumed silicas can contain from 80 to 2000 ppm of aluminum impurity. Such aluminum is typically present as Al2O3 in the silicalite product. While such small

quantities of aluminum may exist, the silicalite containing such alumina or other oxide impurities can in no way be considered to be an aluminosilicate. If such alumina is present in the silica source, however, it may provide a silicalite crystalline structure that provides a silica/alumina molar ratio of about 450:1 or 500:1 or greater, more particularly from about 600:1, 700:1, 800:1, 900:1, 1000:1, 5000:1, 10,000:1 or higher. Silicalites do not have acidity, which limits the cracking of long paraffins contained in the feed. This is advantageous when long paraffins are desired as the final desired products.

When the material having the MFI structure is a silicalite, the selective deposition of the transition metal may be performed e.g. by treating the silicalite such that the transition metal will be prevented from grafting onto the surface of the silicalite and subsequently treating it to create positions inside the pore structure to which the transition metal can graft. This method may involve:
contacting the silicalite with a first compound which grafts onto the surface of the silicalite and to which the transition metal cannot be grafted,
contacting the resulting silicalite with a second compound which grafts inside the pore structure and to which the transition metal can be grafted and
grafting the transition metal to the second compound grafted inside the pore structure.

In some preferred embodiments, the material having the MFI structure is ZSM-5. A ZSM-5 zeolite is a porous material containing an intersecting two-dimensional pore structure with 10-membered oxygen rings. Zeolite materials with such 10-membered oxygen ring pore structures are often classified as medium-pore zeolites. The ZSM-5 zeolite catalysts and their preparation are described in US 3702886, which is herein incorporated by reference. Such ZSM-5 zeolites are aluminosilicates that contain both silicon and aluminum in the crystalline structure.

In some preferred embodiments, the material having the MFI structure is ZSM-5 having a SiO_2/Al_2O_3 ratio of at least 180. Preferably, said SiO_2/Al_2O_3 ratio is at most 300. Such ZSM-5 with a SiO_2/Al_2O_3 ratio of 180-300 has a low acidity and hence reduced external acidity, which promotes the selective deposition of the transition metal(s) inside the pore structure of the MFI structure.

Preferably, ZSM-5 is depleted of external acidity. The depletion of acidity in ZSM-5 limits the cracking of long paraffins contained in the feed. This is advantageous when

long paraffins are desired as the final desired products. The depletion of external acidity promotes the selective deposition of the transition metal(s) inside the pore structure of the MFI structure.

Known methods for the depletion of external acidity include silanization of ZSM-5. This is a process of anchoring of chlorosilane species on the external surface of ZSM-5, which in turn leads to a loss of external acidity, as described in detail in Han et.al., Applied Surface Science Volume 257, Issue 22, p. 9525–9531.

The depletion of external acidity can be determined by the adsorption of Collidine molecules and subsequent characterization with for example Infrared spectroscopy. While interacting with the acid sites of zeolite, collidine gives a signal which can be measured by infrared spectroscopy. Collidine is not able to enter the pores of MFI structure. Hence, it can be determined that the ZSM-5 is depleted of external acidity by the use of the infrared spectroscopy.

Preferably, the conditions in step b) include a pressure of ambient-20 MPa, a temperature of 350-500 °C and a Weight Hourly Space Velocity of 0.1-10 h^{-1}.

The conditions in step b) may include a H_2/HC ratio of 1-20.

The conditions in step b) may be different or same as in step c). Accordingly, the conditions described for step c) may also be applied for step b).

step c)

Step c) involves subjecting the effluent obtained by step b) to a selective ring opening. This is done by contacting the effluent obtained by step b) with a ring opening catalyst comprising a hydrogenation metal in the presence of hydrogen.

In this step, the hydrogenated portion of the partially hydrogenated polyaromatics is cleaved. This results in a short chain alkyl compound and monoaromatics or polyaromatics with one less ring. Any substituents of the polyaromatics and the monoaromatics may be cleaved.

The selective ring opening takes place as hydrocracking.

As used herein, the term “hydrocracker unit” or “hydrocracker” relates to a petrochemical process unit in which a hydrocracking process is performed i.e. a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen; see e.g. Alfke et al. (2007) Oil Refining, Ullmann's Encyclopedia of Industrial Chemistry. The products of this process are saturated hydrocarbons, naphthenic (cycloalkane) hydrocarbons and, depending on the reaction conditions such as temperature, pressure and space velocity and catalyst activity, aromatic hydrocarbons including BTX. The process conditions used for hydrocracking generally includes a process temperature of 200-600 °C, elevated pressures of 0.2-40 MPa, space velocities between 0.1-20 h^{-1}. Hydrocracking reactions proceed through a bifunctional mechanism which requires an acid function, which provides for the cracking and isomerization and which provides breaking and/or rearrangement of the carbon-carbon bonds comprised in the hydrocarbon compounds comprised in the feed, and a hydrogenation function. Many catalysts used for the hydrocracking process are formed by combining various transition metals, preferably selected from Groups 6-11 of the Periodic Table of Elements, or metal sulphides, unsupported or with a solid catalyst support such as alumina, silica, alumina-silica, magnesia and zeolites.

The process conditions used for the selective ring opening generally includes a process temperature of 200-600 °C, elevated pressures of 0.2-40 MPa, and space velocities between 0.1-20 h^{-1}, together with 5-20 wt-% of hydrogen (in relation to the hydrocarbon feedstock), wherein said hydrogen may flow co-current with the hydrocarbon feedstock or counter current to the direction of flow of the hydrocarbon feedstock, in the presence of a dual functional catalyst active for both hydrogenation-dehydrogenation and cracking. The ring opening catalyst used in step c) may be any catalyst composition that combines a hydrogenation function and an acid (cracking) function, either in the form of a mixture of different catalyst components having different catalyst function or in the form of a bifunctional catalyst that combines both the acid and the hydrogenation function in one catalyst component comprised in the catalyst composition. Such ring opening catalysts preferably comprise one or more transition metals, preferably selected from Groups 6-11 of the Periodic Table of Elements. Catalysts used in ring opening step c) generally comprise one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or metal sulphide form supported on an acidic solid such as alumina, silica, alumina-silica, magnesia and zeolites. In this respect, it is to be noted

that the term “supported on” as used herein includes any conventional way to provide a catalyst which combines one or more elements with a catalytic support.

In some preferred embodiments, the ring opening step c) comprises contacting the effluent from step b) in the presence of hydrogen with a ring opening catalyst under ring opening conditions,
wherein said ring opening catalyst comprises one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or metal sulphide form supported on an acidic solid, and
wherein said ring opening conditions comprise a temperature of 200-600 °C and a pressure of 3-35 MPa.

In some preferred embodiments, the ring opening catalyst used in the ring opening step c) is a catalyst comprising elements M and A and zeolite (also referred as M/A/zeolite catalyst)comprising:
0.05-2.5 wt-% of element M, wherein said element M is one or more elements selected from Group 10 of the Periodic Table of Elements;
0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and
an aluminosilicate zeolite having a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150, and
wherein the process conditions in the ring opening step c) comprises a pressure of ambient-20 MPa, a temperature of 350-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

Accordingly, preferred process conditions that may be used in the in the ring opening step c) of the process of the present invention comprise a pressure of ambient-20 MPa, a temperature of 350-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

In some preferred embodiments, the ring opening step is performed at a pressure of ambient-20 MPa, for example at least 0.1 MPa, at least 0.2 MPa, at least 0.3 Mpa or at least 0.4 Mpa and/or at most 20 Mpa, at most 15 MPa, at most 12 MPa or at most 10 Mpa.

In some preferred embodiments, the ring opening step is performed at a temperature of a temperature of 350-500 °C, for example at least 380 °C, at least 400 °C, at least 410 °C or at least 420 °C and/or at most 490 °C, at most 480 °C, at most 470 °C or at most 460 °C.

In some preferred embodiments, the ring opening step is performed at a Weight Hourly Space Velocity of 0.1-10 h^{-1}, for example at least 0.5 h^{-1}, at least 1 h^{-1}, at least 1.5 h^{-1} or at least 2 h^{-1} and/or at most 7 h^{-1}, at most 5 h^{-1}, at most 4 h^{-1} or at most 3 h^{-1}.

In some preferred embodiments, the ring opening step is performed at a H_2/HC ratio of 1-20, for example at least, at least 2, at least 3 or at least 4 and/or at most 17, at most 15, at most 12 or at most 10.

As used herein, the H_2/HC ratio is indicated as a molar ratio.

A preferred catalyst that may be used in the in the ring opening step c) is described herein as a M/A/zeolite catalyst, wherein said element M is one or more elements selected from Group 10 of the Periodic Table of Elements; 0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and an aluminosilicate zeolite having a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150.

Zeolites are well-known molecular sieves having a well-defined pore size. As used herein, the term "zeolite" or "aluminosilicate zeolite" relates to an aluminosilicate molecular sieve. An overview of their characteristics is for example provided by the chapter on Molecular Sieves in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 16, p 811-853; in Atlas of Zeolite Framework Types, 5th edition, (Elsevier, 2001). Preferably, the ring opening catalyst used in the ring opening step comprises a large pore size aluminosilicate zeolite. Suitable zeolites include, but are not limited to, zeolite Y, faujasite (FAU), beta zeolite (BEA), and chabazite (CHA). The term "large pore zeolite" is commonly used in the field of zeolite catalysts. Accordingly, a large pore size zeolite is a zeolite having a pore size of above 6 Å such as 6-8 Å.

The aluminosilicate zeolite used in the in the ring opening step c) may have a SiO_2/Al_2O_3 ratio of 1-150. Means and methods for quantifying the SiO_2 to Al_2O_3 molar ratio of a zeolite are well known in the art and include, but are not limited to AAS

(Atomic Absorption Spectrometer), ICP (Inductively Coupled Plasma Spectrometry) analysis or XRF (X-ray fluorescence). It is noted that the SiO_2 to Al_2O_3 molar ratio referred herein is meant as the ratio in the zeolite prior to being mixed with the binder for forming the shaped body. Preferably, the SiO_2 to Al_2O_3 molar ratio is measured by XRF.

Accordingly, element "M" as used herein is one or more elements selected from Group 10 of the Periodic Table of Elements. Preferably, the M/A/zeolite catalyst comprises 0.5-2 wt-% of element M. All weight percentages of element M as provided herein relate to the amount of element M in relation to the total catalyst composition. Preferably, element M is one or more elements selected from the group consisting of Pd and Pt. Most preferably, element M is Pt.

Accordingly, element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements Preferably, the M/A/zeolite catalyst comprises 0.1-1 wt-% of element A, more preferably 0.25-0.75 wt-% of element A. All weight percentages of element A as provided herein relate to the amount of element A in relation to the total catalyst composition. Selecting a catalyst comprising 0.1-1 wt-% of element A was found to reduce the methane make. Preferably, element A is one or more elements selected from the group consisting of Na, K, Rb, Cs, Mg, Ca, Sr and Ba. More preferably, element A is one or more elements selected from the group consisting of Na, K, Rb and Cs. Most preferably, element A is K.

The catalyst composition as used in the ring opening step c) may comprise further components such as a binder. Known binders include, but are not limited to silica, alumina and clay, such as kaolin. Alumina (Al_2O_3) is a preferred binder. The catalyst composition of the present invention preferably comprises at least 10 wt-%, most preferably at least 20 wt-% binder and preferably comprises up to 40 wt-% binder. The catalyst composition is preferably formed into shaped catalyst particles by any known technique, for instance by extrusion.

Preferably, the catalyst used in the ring opening step c) comprises an aluminosilicate zeolite having a 12-ring structure. These specific aluminosilicate zeolites are well known to the skilled man. An overview of their characteristics is for example provided by the Atlas of Zeolite Framework Types, 5th edition, (Elsevier, 2001). Accordingly, an

aluminosilicate zeolite having a 12-ring structure is an aluminosilicate zeolite wherein the pore is formed by a ring consisting of 12 [SiO_4] or [AlO_4]$^+$ tetrahedra.

Preferably, the catalyst used in the ring opening step c) comprises an aluminosilicate zeolite having super cages having a size of 12-14 Å. Means and methods for preparing zeolites comprising super cages are well-known in the art and comprise zeolite post-treatments such as acid leaching and steaming, among others. (Angew. Chem., Int. Ed. 2010, 49, 10074, ACS nano, 4 (2013) 3698).

Preferably, the aluminosilicate zeolite comprised in the catalyst used in the ring opening step c) is zeolite Y. Depending on the silica-to-alumina molar ratio ("SiO_2/Al_2O_3 molar ratio" or "SiO_2/Al_2O_3 ratio") of their framework, synthetic faujasite zeolites are divided into zeolite X and zeolite Y. In X zeolites the SiO_2/Al_2O_3 ratio is between 2 and 3, while in Y zeolites it is 3 or higher. Accordingly, zeolite Y is a synthetic faujasite zeolite having a SiO_2/Al_2O_3 ratio in their framework of 3 or more. Preferably, the zeolite in the selective alkylation catalyst is in the so-called hydrogen form, meaning that its sodium or potassium content is very low, preferably below 0.1, 0.05, 0.02 or 0.01 wt-%; more preferably presence of sodium is below detection limits. Preferably, the zeolite Y used in the process of the present invention has a SiO_2/Al_2O_3 ratio of 60-100 in the event the catalyst does not comprise the optional element A and preferably has a SiO_2/Al_2O_3 ratio of 5-25 in the event the catalyst comprises at least 0.1 wt-% of element A. Preferably, the partially dealuminated zeolite is prepared by controlling SiO_2/Al_2O_3 ratio during zeolite synthesis. Alternatively, the zeolite may be partially dealuminated by a post-synthesis modification. Means and methods to obtain dealuminated zeolite by post-synthesis modification are well-known in the art and include, but are not limited to the acid leaching technique; see e.g. Post-synthesis Modification I; Molecular Sieves, Volume 3; Eds. H. G. Karge, J. Weitkamp; Year (2002); Pages 204-255.

A preferred catalyst that may be used in the in the ring opening step c) is described herein as a M/A/zeolite catalyst, wherein said element M is one or more elements selected from Group 10 of the Periodic Table of Elements; 0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and an aluminosilicate zeolite having a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150.

In some preferred embodiments, the ring opening catalyst is a M/A/zeolite catalyst, wherein the catalyst comprises a shaped body comprising a zeolite and an optional binder and elements M/A deposited on the shaped body. Preferably, the process conditions in step c) include a pressure of ambient to 5 MPa, for example at least 0.1 MPa, at least 0.2 MPa, at least 0.3 Mpa or at least 0.4 Mpa and/or at most 5 Mpa or at most 4 Mpa.

In some preferred embodiments, the ring opening catalyst the ring opening catalyst is a M/A/zeolite catalyst, wherein the catalyst comprises a mixture of a binder and elements M/A deposited on the binder and a zeolite. Preferably, the process conditions in step c) include a pressure of 1 to 20 MPa, for example at least 2 MPa, at least 3 MPa, at least 4 Mpa or at least 5 Mpa and/or at most 15 Mpa or at most 10 Mpa.

The effluent obtained by step c) comprises monoaromatics. The monoaromatics may be separated out as the product of the process of the invention. Any remaining polyaromatics may be recycled through the process.

reactors

Steps b) and c) may be performed in the same reactor or different reactors. The use of the same reactor is advantageous in terms of CAPEX.

When steps b) and c) are performed in the same reactor, the dehydrogenation catalyst and the aromatic opening catalyst are positioned such that dehydrogenation takes place before the aromatic opening. When steps b) and c) are performed in the same reactor, the conditions in steps b) and c) may be the same. However, a higher ratio of H2/hydrocarbon in step b) leads to a lower conversion of cyclohexane to benzene. Hence, it is preferred that the injection of hydrogen into the reactor is performed such that H_2/HC ratio in step b) is lower than H_2/HC ratio in step c). This can be done by injecting hydrogen into the reactor after the location of the dehydrogenation catalyst.

When steps b) and c) are performed in different reactors, it is preferred that no hydrogen is injected in the reactor for step b).

Experiments

Experiment set 1: reactivity between monoaromatics and single ring naphthenics

A feed composition as shown in Table 1 was subjected to a selective ring opening (= step c) of the present invention) at two different WHSV. The catalyst used was a physical mixture (1:1 weight ratio) of Al2O3 particles onto which Pt is deposited (Pt =0.75 wt% with respect to the total of Al2O3 particles and Pt), and Zeolite Y with a SiO2/Al2O3 ratio of 80.

Table 1. Model feed composition

Model Feed	
Decane	25 wt%
Propylbenzene	20 wt%
Naphthalene	25 wt%
1-Methylnaphthalene	15 wt%
2-Methylnaphthalene	10 wt%
Anthracene	2 wt%
Phenantrene	3 wt%

The conditions of the selective ring opening and the compositions of the effluents are summarized in Table 2.

Table 2 Effluent compositions

	Ex 1	Ex 2
P (bara)	60	60
T (°C)	450	450
WHSV	2	4
Component (wt%)	Effluent	Effluent
n-propylbenzene	3.7	11.7
Di-aromatics	1.4	7.7
Tri-Aromatics	0	0.1
Conversion		
n-propylbenzene	81.4	41.7
Di-aromatics	93	61.5
Tri-Aromatics	100	99.5

It can be seen from Table 2 that the reactivity of monoaromatics is reduced to a higher extent when the contact time is decreased (higher WHSV) as compared to the decrease in the reactivity of polyaromatics.

This holds true for the opposite reaction: the conversion of single ring naphthenic species into monoaromatics is reduced to a higher extent when the contact time is decreased (higher WHSV) as compared to that of multiple ring naphthenic species. Hence, it can be understood that the reactivity of single ring naphthenic species into monoaromatics is hindered by the presence of multiple ring naphthenic species.

Therefore, the catalyst in step b) has to be chosen such that the dehydrogenation sites are available exclusively for single ring naphthenic species and not for naphthenic species with more than one ring. This will limit the competition effects between single ring naphthenic species and multiple ring naphthenic species.

Experiment set 2: effect of H2/HC ratio

A series of Aspen simulations have been conducted to show the effect exerted by the H2:hydrocarbon ratio and pressure conditions in the dehydrogenation equilibrium of cyclohexane. This has been performed using the Peng Robinson thermodynamic equation. Conditions and results are shown in Tables 3 and 4.

Table 3

	H2/HC 10		H2/HC 5		H2/HC 3		H2/HC 2	
	Inlet	outlet	Inlet	outlet	Inlet	outlet	Inlet	outlet
Temperature C	400	450	400	450	400	450	400	450
Pressure bar	30	30	30	30	30	30	30	30
Mole Flow kmol/hr								
Hydrogen	10	10.276	5	5.379	3	3.473	2	2.548
Cyclohexane	0.3	0.208	0.3	0.174	0.3	0.142	0.3	0.117
Benzene	0.7	0.792	0.7	0.826	0.7	0.858	0.7	0.883

	H2/HC 10		H2/HC 5		H2/HC 3		H2/HC 2	
	Inlet	outlet	Inlet	outlet	Inlet	outlet	Inlet	outlet
Temperature C	400	450	400	450	400	450	400	450
Pressure bar	60	60	60	60	60	60	60	60
Mole Flow kmol/hr								
Hydrogen	10	8.88	5	4092	3	2357	2	1.608
Cyclohexane	0.3	0.673	0.3	0.603	0.3	0.514	0.3	0.431
Benzene	0.7	0.327	0.7	0.397	0.7	0.486	0.7	0.569

Table 3 shows that the conversion of cyclohexane to benzene is increased when H2/hydrocarbon ratio is decreased. Same trend can be understood from Table 4.

Therefore, when the ratio of H2/hydrocarbon to be used in the process is fixed and steps b) and c) are performed in the same reactor, a higher conversion of cyclohexane to benzene can be obtained by injecting H2 after the location of the dehydrogenation catalyst.

Experiment set 3: aromatic opening catalysts

The transformation of heavy hydrocarbon streams was investigated using a model feed that mimics Light Cycle Oil (LCO) composition in terms of triaromatics, diaromatics, monoaromatics and paraffin content. The model feed was hydrocracked using different types of catalysts. This was performed at a hydrogen to hydrocarbon ratio of 10 and a WHSV of 1 h^{-1}.

Table 4 Model feed composition details.

Model Feed	
Decane	25 wt%
Propylbenzene	20 wt%
Naphthalene	25 wt%
1-Methylnaphthalene	10 wt%
2-Methylnaphthalene	15 wt%
Anthracene	2 wt%
Phenantrene	3 wt%

Physical mixture Pt/Al2O3 + Zeolite Y

The aromatic ring opening catalyst was mixture of Al2O3 particles on which Pt is deposited and zeolite. It was composed of commercially available catalyst samples: One part of the catalyst is a Pt/Al_2O_3 from UOP, namely R-12. The zeolite was an unmodified zeolite Y from Zeolyst, namely CBV 780. These samples were mixed in a 1 to 1 ratio.

Pt/Zeolite Y

65 grams of Zeolyst CBV 780 was divided into 3 ceramic dishes and calcined in air at 100°C for 3 hours to 300°C and then to 550°C for 10 hours using a ramp rate of 3°C/min.

After calcination, 15 grams of pre-dried sample was dispersed in 1 liter of deionized water and stirred at 65°C overnight. The next day the temperature was raised to 70°C and a solution of 0.317g of $Pt(NH_3)_4 (NO_4)_2$ was dissolved in 76.4 g of DI-H_2O and added drop wise over a period of 7 hours. The material was allowed to stir overnight at 70°C prior to filtering off the liquid. The filter cake was re-suspended in 1 liter of fresh DI-H_2O and allowed to stir for 15 min and subsequently filtered again. The washing step was repeated twice more. The material was then allowed to dry overnight on filter paper at room temperature. Next, the material was dried at 80°C for 3 hours , pressed (10,000 psi), crushed and sieved (35-60 mesh sizing scheme). The sized material was loaded in a tube furnace with an air flow rate of 2.2 L/min. The furnace was heated to 100°C for 3 hours then to 300°C for 3 hours at a ramp rate of 0.2°C /min.

Subsequently, the material was further calcined to 350°C at 0.2°C /min for 3 hours. The flows rates were then turned down to down to 1L/min for 1 hour then to 345 ml/min for

1 hour while 350°C is maintained. The material was then transferred to the calcination oven and calcined for 3 hours in air using the same ramp rate of 0.2°C /min

Pt/K/Zeolite

24 grams of pre-dried CBV 712 was suspended in 2 liters of deionized water (DI-H_2O) and stirred at 40°C overnight. Next day the temperature was raised to 70°C and a solution of 0.602g of $Pt(NH_3)_4(NO_4)_2$ was dissolved in 123.33 g of DI-H_20 and added drop wise over a period of 5 hours. The material was allowed to stir overnight at 70°C prior to filtering off the liquid. The filter cake was re-suspended in 1 liter of fresh DI-H_20 and allowed to stir for 15 minutes before filtering it again. This washing step was repeated twice more. The material was then allowed to dry at room temperature over the weekend. Next the material was pressed (10,000 psi), crushed and sieved through a 35-60 mesh sizing scheme. The sized material was loaded in a tube furnace with an air flow rate of 2.2 L/min. The furnace was heated to 100°C for 3 hours then to 300°C for 3 hours at a ramp rate of 0.2°C /min. Subsequently, the material was further calcined to 350°C at 0.2°C /min for 3 hours. The flows rates were then turned down to down to 1L/min for 1 hour then to 345 ml/min for 1 hour while 350°C was maintained. The material was then transferred to the calcination oven and calcined for 3 hours in air using the same ramp rate of 0.2°C /min.

12 grams of the above described Pt/Zeolite Y catalysts was predried, weighed and added to 0.342 g of KNO_3 dissolved in 700 ml of DI-H_20. The material was stirred for 7 hours at 65°C. The material was then filtered and rinsed with 150 ml of fresh DI-H_2O directly on the filter cake. The material was subsequently transferred to a ceramic dish and dried for 3 hours at 100 then calcined in air at 300°C for 3 hours using a ramp rate of 0.2°C /min.

Table 5

		monoaromatics (BTX)	LPG
mixture (Pt/Al2O3 and zeolite)	450°C/3MPa	28.2 (8.7)	9.4
Pt/K/zeolite	450°C/3MPa	34.7 (20.6)	18
Pt/zeolite	450°C/3MPa	33.6 (22.6)	28.3

At 3 MPa, the hydrocracking using a catalyst in which Pt (and K) was deposited on zeolite and Al2O3 resulted in more monoaromatics. In particular, the amount of BTX obtained by Pt(K)/zeolite was much higher than that by the mixture. Similar trend was observed at a temperature of 400 °C and 30 bar.

Similar experiments performed at a pressure of 6 MPa led to a result in which the mixture resulted in more monoaromatics since the compositions obtained from Pt(K)/zeolite led to a large amount of LPG.

CLAIMS

1. A process for producing monoaromatics from a hydrocarbon feed comprising polyaromatics and monoaromatics, comprising
   a) contacting the hydrocarbon feed in the presence of hydrogen with a hydrotreatment catalyst for reducing sulfur and nitrogen components and saturating at least one of the aromatic rings of the polyaromatics in the hydrocarbon feed to obtain partially dehydrogenated polyaromatics,
   b) contacting the effluent obtained by step a) with a selective dehydrogenation catalyst for selectively dehydrogenating single ring naphthenic species in the effluent obtained by step a), wherein the dehydrogenation catalyst comprises an aluminosilicate or a silicate material having a mordenite framework inverted (MFI) structure wherein one or more transition metals are selectively deposited inside pore structure of the MFI structure and
   c) contacting the effluent obtained by step b) in the presence of hydrogen with a ring opening catalyst for opening saturated aromatic rings of the partially dehydrogenated polyaromatics in the effluent obtained by step b).
2. The process according to claim 1, wherein the hydrocarbon feed comprises at least 10 wt-% polyaromatics, preferably at least 20 wt-% polyaromatics and most preferably at least 30 wt-% polyaromatics.
3. The process according to any one of the preceding claims, wherein in step a), at least 60, preferably at least 75, more preferably at least 85 wt% of the polyaromatics have one aromatic ring fully saturated.
4. The process according to any one of claims 1-3, wherein the material having the MFI structure is silicalite-1.
5. The process according to any one of claims 1-3, wherein the material having the MFI structure is ZSM-5.
6. The process according to claim 5, wherein the material having the MFI structure is ZSM-5 having a SiO_2/Al_2O_3 ratio of 180-300 and depleted of external acidity.
7. The process according to any one of the preceding claims, wherein the hydrotreatment catalyst comprises 0.0001 to 5 wt% of one or more metals selected from the group consisting of Ni, W, and Mo based on the total weight of the catalyst.
8. The process according to any one of claims 1-7, wherein the ring opening catalyst comprises one or more elements selected from the group consisting of Pd, Rh, Ru, Ir, Os, Cu, Co, Ni, Pt, Fe, Zn, Ga, In, Mo, W and V in metallic or

metal sulphide form supported on an acidic solid, and
wherein said ring opening conditions comprise a temperature of 200-600 °C and a pressure of 3-35 MPa.

9. The process according to any one of claims 1-7, wherein the ring opening catalyst is a catalyst comprising elements M and A and zeolite comprising:
0.05-2.5 wt-% of element M, wherein said element M is one or more elements selected from Group 10 of the Periodic Table of Elements;
0-1 wt-% of element A, wherein said element A is one or more elements selected from Group 1 and 2 of the Periodic Table of Elements; and
an aluminosilicate zeolite having a pore size of 6-8 Å and a SiO_2/Al_2O_3 ratio of 1-150, and
wherein the process conditions in the ring opening step c) comprises a pressure of ambient-20 MPa, a temperature of 350-500 °C, a Weight Hourly Space Velocity of 0.1-10 h^{-1} and a H_2/HC ratio of 1-20.

10. The process according to claim 9, wherein the ring opening catalyst comprises a shaped body comprising a zeolite and an optional binder and elements M/A deposited on the shaped body.

11. The process according to claim 10, wherein the process conditions in step c) include a pressure of ambient to 5 MPa, for example at least 0.1 MPa, at least 0.2 MPa, at least 0.3 Mpa or at least 0.4 Mpa and/or at most 5 Mpa or at most 4 Mpa.

12. The process according to claim 9, wherein the ring opening catalyst comprises a mixture of a zeolite and a binder and elements M/A deposited on the binder.

13. The process according to claim 10, the process conditions in step c) include a pressure of 1 to 20 MPa, for example at least 2 MPa, at least 3 MPa, at least 4 Mpa or at least 5 Mpa and/or at most 15 Mpa or at most 10 Mpa.

14. The process according to any one of the preceding claims, wherein steps b) and c) are performed in a single reactor and the injection of hydrogen into the reactor is performed such that H_2/HC ratio in step b) is lower than H_2/HC ratio in step c).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/080628

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G45/08 C10G65/04 C10G65/12 C10G45/50 C10G45/70
C10G45/44 C10G45/46 C10G65/08
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 January 2017	03/02/2017

Name and mailing address of the ISA/	Authorized officer
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1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/080628

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR 2 087 391 A5 (INST FRANCAIS DU PETROLE) 31 December 1971 (1971-12-31) page 1, lines 1-4 page 3, lines 16-36 page 4, lines 5-27 page 5, lines 15-33 page 10, lines 5-6,24-25	1-14
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1

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Information on patent family members

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