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Process for the production of aromatic hydrocarbons from aliphatic hydrocarbons.

Aromatic hydrocarbons are produced by catalytic conversion of aliphatic hydrocarbons using an aluminogallosilicate catalyst. A feed of the aliphatic hydrocarbon is mixed with a recycle gas and the mixture is contacted with the catalyst. The resultant conversion product is separated into a gas phase and a liquid phase containing aromatic hydrocarbons. The gas phase is separated into a hydrogen-rich gas and a methane- and/or ethane-rich gas while the liquid phase is separated into an aromatic hydrocarbon-containing product and a light hydrocarbon-containing gas. At least part of the methane- and/or ethane-rich gas and the light hydrocarbon-containing gas is recycled as the above recycle gas. The catalytic conversion is performed while increasing the reaction temperature as the process proceeds.

This invention relates to a process for the production of aromatic hydrocarbons from an aliphatic hydrocarbon raw material containing one or more olefins and/or paraffins having 2-7 carbon atoms.

It is well known that aromatic hydrocarbons may be produced by catalytic conversion of an aliphatic hydrocarbon having 2-7 carbon atoms. Proton-type ZSM-5, a proton-type aluminosilicate of an MFI structure having loaded thereon Ga by impregnation or ion-exchange, a proton-type gallosilicate of an MFI structure, a proton-type or ammonium-type aluminogallosilicate of an MFI structure modified by treatment with steam, and a proton-type, crystalline aluminogallosilicate have been used as the conversion catalyst.

Known processes for the catalytic conversion of light hydrocarbons into aromatic hydrocarbons have a problem that the activities of the catalysts are relatively easily reduced due to the deposition of coke on the catalysts so that the aromatics yield is decreased as the process proceeds. As a result, the composition of the product varies with time so that it is very difficult to optimize the entire process conditions.

European publication EP-A-0400987 discloses a process for the production of high-octane gasoline by conversion of a light hydrocarbon using particulate crystalline aluminogallosilicate and suggests to separate a light fraction containing methane and ethane as major ingredients from the conversion product and to recycle the separated fraction to the catalytic conversion step. While this process gives an improvement in activity retentivity of the catalyst, it has been found that, with this process, it is difficult to maintain the aromatics yield at a desired high level.

In accordance with the present invention there is provided a process for the production of aromatic hydrocarbons from an aliphatic hydrocarbon having 2-7 carbon atoms, comprising the steps of:

- (a) mixing a feed of an aliphatic hydrocarbon having 2-7 carbon atoms with a recycle gas to obtain a first mixture;
- (b) contacting said first mixture with an aluminogallosilicate catalyst to convert the aliphatic hydrocarbon into aromatic hydrocarbons and to obtain a second mixture containing the aromatic hydrocarbons;
- (c) separating said second mixture into a gas phase and a liquid phase containing aromatic hydrocarbons;
- (d) separating said gas phase into a first gas mixture rich in hydrogen and a second gas mixture rich in methane and/or ethane;
- (e) separating said liquid phase into an aromatic hydrocarbon-containing product and a light hydrocarbon-containing gas; and
- (f) recycling at least part of said second gas mixture and said light hydrocarbon-containing gas to step (a) as said recycle gas, the temperature at which step (b) is performed being increased as the process proceeds to maintain the aromatics yield R within the range of 40-75 %, wherein R is defined as follows:

$$R = A/B \times 100 (\%)$$

where A is the weight of the aromatic hydrocarbons contained in said second mixture and B is the weight of the aliphatic hydrocarbons which has 2-7 carbon atoms, which are contained in said aliphatic hydrocarbon feed and which are other than ethane.

The present invention will now be described in detail below with reference to the accompanying drawing, in which the sole FIGURE is a flow diagram showing one preferred embodiment according to the present invention.

The term "feed of an aliphatic hydrocarbon having 2-7 carbon atoms" used herein is intended to refer to a raw material for the preparation of aromatic hydrocarbons which contains one or more paraffins and/or olefins with carbon atoms ranging from 2 to 7 as a major constituent. Representative of the aliphatic hydrocarbon is a light fraction having boiling points of 100 °C or lower and obtainable from naphtha fractions containing paraffins with carbon atoms ranging from 5 to 7 as a major constituent.

The catalyst to be used in the process of the present invention is a crystalline aluminogallosilicate whose skeleton is comprised of SiO₄, AlO₄ and GaO₄ tetrahedra and which may be produced by the gel crystallization method using hydrothermal synthesis or by the method of inserting gallium into the lattice skeleton of an aluminosilicate or inserting aluminum into the lattice skeleton of a gallosilicate.

The gel crystallization method is simpler because an objective quantity of aluminum and gallium can be contained at the same time in the preparation of the crystalline aluminogallosilicate. A crystalline aluminogallosilicate may be produced by this method by subjecting a finely divided aqueous mixture containing a silica source, an alumina source and a gallia source as an essential constituent, in addition to a constituent necessary for the silicate synthesis, to conditions for the hydrothermal synthesis.

As sources of silica may be used, for example, a silicate such as sodium silicate or potassium silicate, colloidal silica, silica powder, dissolved silica and water glass. As sources of alumina are used, for example, an aluminum salt such as aluminum sulfate or aluminum nitrate, an aluminate such as sodium aluminate, and aluminum gel. As sources of gallia are used, for example, a gallium salt such as gallium nitrate or gallium chloride, and gallium oxide. As a further source of alumina or gallia, there may be used a solution or a hydroxide containing aluminum or gallium obtainable during the extraction or purification step of a deposit such as a

bauxite deposit, zinc deposit or the like.

An organic additive may also be used in order to accelerate the growth of a desired crystalline aluminogallosilicate and to improve the purity thereof, thus yielding products of better quality. As organic additives useful in this method are, for example, quaternary ammonium salts such as tetrapropylammonium salt, a tetrabutyl-

ammonium salt or a tripropylmethylammonium salt, an amine such as propylamine, butylamine, aniline, dipropylamide, dibutylamide or morpholine, an aminoalcohol such as ethanolamine, diglycolamine or diethanolamine, an alcohol such as ethanol, propylalcohol, ethylene glycol or pinacol, an ester, an organic acid, an ether, a ketone, an amino acid, a thioalcohol and a thioether. A compound that produces such organic additives under the hydrothermal synthesis conditions may also be used.

As a source of an alkali metal or an alkaline earth metal, there may be used, for example, a hydroxide, a halide, a sulfate, a nitrate or a carbonate of an alkali metal such as sodium or potassium or an alkaline earth metal such as magnesium or calcium. The raw material may contain a mineral acid such as sulfuric acid or nitric acid as a pH adjusting agent, in addition to the above-described compounds.

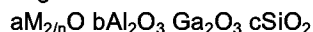
An aqueous mixture containing one or more of the above-described compounds to be used as a raw material may be subjected to crystallization at temperatures from 50 °C to 300 °C, preferably from 150 °C to 250 °C under autogenous pressures for a retention period of from about 1 hour to 7 days, preferably from 2 hours to 5 days. The product obtained by the above-mentioned process may be further subjected to conventional activation or modification treatment as needed. Accordingly, the crystalline aluminogallosilicate referred to herein may also include a variety of modified and/or activated products obtainable by the modification and/or activation treatments in addition to those producible by hydrothermal synthesis.

In the production of crystalline aluminogallosilicate by hydrothermal synthesis, the particle size of the product depends upon a lot of factors such as the kind of the silica source, the amount of organic additives (e.g. quaternary ammonium salt), the amount and kind of the inorganic salt to be used as a mineralizer, the amount of base in the gel, the pH of the gel, the temperature of the crystallization and the rate of stirring. By appropriately controlling these conditions, crystalline aluminogallosilicate having a particle size of about 0.05-20 µm with at least 80 % by weight thereof having a particle size of 0.1-10 µm may be produced.

An MASNMR (Magic Angle Spinning Nuclear Magnetic Resonance) analysis may directly or indirectly give useful information on the elements present in the crystal structure of the crystalline aluminogallosilicate and on the composition thereof. For example, the ²⁷Al-NMR analysis of a crystalline aluminosilicate gives information on aluminum of the tetrahedral configuration in the anionic skeletal structure. The ²⁹Si-NMR analysis gives information on the four tetrahedra (TO₄; T = Al, Ga, Si) adjacent to the SiO₄ tetrahedron in the structure thereof. In the aluminogallosilicate according to the present invention, the ²⁷Al-NMR and ⁷¹Ga-NMR analyses show that the Al and Ga elements of the tetrahedral configuration are present in the skeletal structure. From information provided by the ²⁹Si-NMR analysis, the mole ratio of SiO₂ to (Al₂O₃ + Ga₂O₃) in the crystal structure is computed. The results are in well conformity with those obtained from elementary analysis.

One of the chemical characteristics of the crystalline aluminogallosilicate is its acid property. Generally, the degree of acidity may be determined by means of the temperature programmed desorption or the measurement for heat of adsorption using basic substance such as ammonia or pyridine. As the degrees of acidity balancing the aluminum and gallium used for synthesis are measured in the aluminogallosilicates, it is apparent that the aluminum and gallium are present in the anionic skeletal structure of the crystal structure.

In the crystalline aluminogallosilicate to be used as a catalyst component in the process of the present invention the skeletal structure thereof preferably has an aluminum content of 0.1-2.5 % by weight and a gallium content of 0.1-5 % by weight. The aluminogallosilicate has a SiO₂/(Al₂O₃ + Ga₂O₃) molar ratio of 17-606, preferably 19-200, a SiO₂/Al₂O₃ molar ratio of 32-870, preferably 35-300 and a SiO₂/Ga₂O₃ molar ratio of 36-2,000, preferably 40-500 and preferably has a composition represented by the following formula in terms of molar ratios of the oxides when calcined at 500 °C or higher:



wherein M represents a metal selected from the group consisting of alkali metals, alkaline earth metals and mixtures thereof, n represents the valence of said metal M, a is a positive number of (b+1)⁻³, preferably (b+1)⁻², b is a number of 0.04-62.5, preferably 0.1-14.0 and c is a number of 36-2,000, preferably 40-500 and wherein at least a portion of said metal M is optionally replaced by proton.

Most preferable crystalline aluminogallosilicates are of the MFI type and/or of the MEL type. The MFI type and MEL type silicates belong to the structural type of the known zeolites of the kind published in "The Structure Commission of the International Zeolite Association" (Atlas of Zeolite Structure Types, W. M. Meier and D. H. Olson (1978), Distributed by Polycrystal Book Service, Pittsburgh, PA, USA).

The particle size of the crystalline aluminogallosilicate to be used in the present invention is about 0.05-20 µm. It is important that at least 80 % by weight of the crystalline aluminogallosilicate should have a particle

size of 0.1-10 μm in order for the catalyst to exhibit a desired activity retentivity and other catalytic activities. Preferably at least 80 % by weight of the crystalline aluminogallosilicate has a particle size of 0.5-5 μm , more preferably 1-3 μm . The crystalline aluminogallosilicate is in the form of aggregated particles (secondary particles) composed of primary particles having a particle size of about 0.02-2 μm .

When the crystalline aluminogallosilicate is prepared by hydrothermal synthesis, it is preferable to use a crystallization temperature of at least 140 $^{\circ}\text{C}$, more preferably 150-250 $^{\circ}\text{C}$ for reasons of obtaining high catalytic activity. A crystallization temperature of below 140 $^{\circ}\text{C}$ is economically disadvantageous because a long crystallization time is required for obtaining similar effects. Additionally, it is not recommendable to maintain the reaction mixture in the hydrothermal synthesis conditions for a long period of time, since the zeolite crystal phase is in a quasi-stable state in such an environment so that there is an increased danger of contamination with undesirable phases.

When the particle size of the aluminogallosilicate exceeds 20 μm , distribution of Si, Al and Ga crystallites becomes ununiform, resulting in deterioration of catalytic activity thereof. Further, since a diffusion rate of reactant molecules in pores of the zeolite structure, which pores have the same diameter as that of the molecules, is slow, the reactant molecules are hard to access to catalytically active sites located in the depth of the pores when the particle size exceeds 20 μm . Thus, the active sites are not effectively used for the conversion reaction. Moreover, deposition of coke on outer surfaces of the catalyst causes blocking or plugging of the pores of the silicate, so that active sites in the depth of the pores are not effectively used. Reduction of the yield and selectivity in the case of the catalyst with the large particle size aluminogallosilicate is considered to be attributed to the above.

The catalytic activity of the aluminogallosilicate also depends on the composition thereof. In order to obtain high catalytic activity, it is important that the aluminogallosilicate should contain, in its skeletal structure, 0.1-2.5 % by weight, preferably 0.1-2.0 % by weight of aluminum, 0.1-5.0 % by weight, preferably 0.1-2.5 % by weight of gallium. It is also preferred that the silicate have a $\text{SiO}_2/\text{T}_2\text{O}_3$ ($\text{T}_2\text{O}_3 = \text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3$) molar ratio of 25-200 for reasons of good retentivity of high catalytic activity for a long period of time.

The above crystalline aluminogallosilicate is used in the form of a mixture with a binder as a catalyst for the production of high-octane gasolines. The binder serves to improve mechanical properties such as strength, wear resistance and moldability. Illustrative of suitable binders are alumina, silica, aluminoboria, silicaalumina and the like inorganic oxides. The content of the binder in the catalyst is generally 10-70 % by weight. Addition of phosphorus to these inorganic binders can further improve mechanical strengths of the molded catalysts.

A mixture of the silicate and the binder is formulated as a cylindrical shape, a granule, a sphere, a sheet, a pellet or the like shape by means of extrusion molding, spray drying, tableting press, tumbling or an oil drop method. To facilitate the molding, an organic lubricant may be advantageously used.

The aluminogallosilicate catalyst may be subjected to activation treatments commonly adopted for conventional zeolite catalysts, as desired. For example, the silicate catalyst may be converted into an ammonium form by ion exchange in an aqueous solution containing an ammonium salt such as ammonium chloride, ammonium nitrate, ammonium fluoride, ammonium hydroxide or the like. The ammonium-form catalyst may further be subjected to ion exchange treatment or impregnation treatment in an aqueous solution containing ions of a desired metal other than alkali metals and alkaline earth metals for the introduction of the desired metals into the catalyst. The aluminogallosilicate catalyst in the ammonium form may also be converted into an acid form by calcination in the atmosphere of air, nitrogen or hydrogen at 200-800 $^{\circ}\text{C}$, preferably 350-700 $^{\circ}\text{C}$ for 3-24 hours. The acid catalyst may be further treated with hydrogen or a mixture of nitrogen and hydrogen under the above conditions. The above activation treatment is generally performed for the catalyst prior to the initiation of the catalytic conversion of a light hydrocarbon raw material into aromatic hydrocarbons. Alternatively, the treatment may be carried out for the aluminogallosilicate which has not yet been molded with a binder into a desired shape.

The aluminogallosilicate catalyst in the proton form is advantageously used. The proton type catalyst may further contain, as an auxiliary catalytic component, one or metals capable of improving dehydrogenation activity or of preventing coke deposition. Examples of the auxiliary catalytic metal include magnesium, calcium, strontium, barium, lanthanum, cerium, titanium, vanadium, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, tin, aluminum, indium, germanium, zinc, gallium, lead, phosphorus, antimony, bismuth and selenium. These metals may be used singly or in combination of two or more.

The amount of the auxiliary metal to be supported on the catalyst is generally 0.01-10 % by weight in terms of elemental metal. The supported catalyst may be prepared by any known method such as ion-exchange or impregnation. The auxiliary metal component may be incorporated into the catalyst by supporting the metal component on the binder with which the aluminogallosilicate is to be molded or on the molded catalyst. Further, the auxiliary metal component may be added in a reaction mixture for the preparation of crystalline aluminogallosilicate.

Illustrative of suitable auxiliary metals which are effective to prevent coke deposition are magnesium, calcium, lanthanum, cerium, ruthenium and iridium. The metal component is generally used in an amount of 0.01-5 % by weight in terms of elemental metal.

Referring now to the FIGURE, a feed of the aliphatic hydrocarbon having 2-7 carbon atoms is supplied through a line 7 and is mixed with a hereinafter described recycle gas supplied through a line 17. The resulting mixture (first mixture) is then supplied through a line 18 to a reaction zone 1 where the mixture is contacted with a bed of the above aluminogallosilicate catalyst.

The conversion of the aliphatic hydrocarbon into aromatic hydrocarbon is suitably carried out at a temperature of 350-650 °C under a partial hydrogen pressure of 5 kg/cm² or less. The reaction temperatures may range more preferably from 450 °C to 650 °C for the aliphatic hydrocarbons containing a n-paraffin as a major constituent, from 400 °C to 600 °C for the aliphatic hydrocarbons containing an isoparaffin as a major constituent, and from 350 °C to 550 °C for the aliphatic hydrocarbons containing an olefin as a major constituent.

It is important that the reaction temperature in the conversion step should be controlled so as to obtain an aromatics yield within a predetermined range. For this purpose, the reaction temperature is stepwisely (discontinuously) or continuously increased with time. When the aromatics yield is no longer controllable within a predetermined range by increase of the reaction temperature, the catalyst should be renewed. The spent catalyst can be regenerated by heating at 200-800 °C, preferably 350-700 °C in the atmosphere of air, nitrogen, hydrogen or a mixture of nitrogen and hydrogen. This heat treatment may be performed in the reactor or in a separate regeneration zone.

The aromatics yield R is defined as follows:

$$R = A/B \times 100 (\%)$$

where A is the weight of the aromatic hydrocarbons contained in the product discharged from the reaction zone 1 and B is the weight of the aliphatic hydrocarbons having 2-7 carbon atoms (except ethane) contained in the aliphatic hydrocarbon feed supplied through the line 7.

In the process of the present invention, the aromatics yield R is controlled within the range of 40-75 %, preferably 45-70 %.

The process of the present invention is preferably carried out using two groups of reaction towers each containing the above aluminogallosilicate catalyst. Each of the two groups is composed of a plurality of reaction towers connected in series. The aliphatic hydrocarbon feed is fed to one of two groups of reaction towers while the other group of reaction towers is subjected to regeneration treatment. By using the two groups of reactors alternately by switching valves, the process can be performed continuously for a long period of time, for example, for one year or more. In this case, it is desirable to conduct the valve switching at an interval of 1-10 days. In each cycle of the 1-10 days reaction, the reaction temperature is independently increased, preferably by 5-20 °C, to maintain the aromatics yield within the desired range.

As reactions including the dehydrogenation proceed in the conversion of the light hydrocarbons to the aromatic hydrocarbons, the hydrogen partial pressures balancing the reaction can be attained without an addition of hydrogen. An intentional addition of hydrogen may have the advantages that the coke accumulation can be prevented and the catalyst life can be prolonged, but it is not necessarily advantageous because an increase of the hydrogen partial pressure may radically decrease the yields of the aromatic hydrocarbons. It is accordingly preferred to restrict the hydrogen partial pressures to 5 kg/cm² or lower.

It is important that a methane- and/or ethane-containing light hydrocarbon gas separated in the separation step (in zones 5 and 6) described hereinafter should be present in the conversion step in order to prevent coke deposition on the catalyst and to maintain the aromatics yield at a high level for a long period of time. Thus, the methane-containing light hydrocarbon gas separated in the separation step is mixed with the aliphatic hydrocarbon raw feed and the mixture is fed to the reaction zone 1. The amount of the methane-containing light hydrocarbon gas to be recycled to the reaction zone 1 is generally 0.1-10 parts by weight, 0.5-3 parts by weight per part by weight of the fresh, light hydrocarbon raw material feed.

The catalytic conversion may be performed using a fixed bed system, a moving bed system or a fluidized bed system. The feed rate of the light hydrocarbon raw material feed is generally 100-2,000 hour⁻¹ in terms of gas space velocity when a fixed bed system is adopted. In the case of other systems, the contact time is determined so as to obtain suitable aromatics yield.

The thus obtained reaction mixture (second mixture) containing aromatic hydrocarbons and discharged from the reaction zone 1 through a line 8 is introduced into a gas-liquid separation zone to separate the reaction mixture into a gas phase and a liquid phase containing aromatic hydrocarbons. Preferably, the reaction mixture is cooled by indirect heat exchange with the first mixture flowing through the line 18 before being fed to the separation zone. The separation is performed at a temperature of 10-50 °C, preferably 20-40 °C, and a pressure of 5-80 atm, preferably 10-30 atm.

The gas-liquid separation zone in the illustrated embodiment is composed of three, low, medium and high

pressure separation towers 2, 3 and 4. The reaction mixture is first introduced into the low pressure separation tower 2 where it is separated into a first gas phase and a first liquid phase. The first gas phase is fed through a line 19 to the medium pressure separation tower 3 after being pressurized, so that the first gas phase is separated into a second gas phase and a second liquid phase. The second gas phase is discharged from the tower 3 and is fed, after being further pressurized, to the high pressure separation tower 4 through a line 20. The second liquid phase is recycled through a line 21 into the low pressure separation tower 2. The first liquid phase is discharged from the low pressure separation tower 2 and is fed, after being pressurized, to the high pressure separation tower 4 together with the pressurized second gas phase from the tower 3. In the tower 4, the mixed feed is separated into a third gas phase containing hydrogen, methane, ethane, butane and other light hydrocarbons and a third liquid phase containing aromatic hydrocarbons as a major component. The third gas and liquid phases are discharged from the separation tower 4 through lines 11 and 10, respectively. The low and/or medium pressure separation towers may be omitted. However, the use of two or more separation towers is recommendable.

The gas phase (third gas phase) obtained in the separation zone (high pressure separation tower 4, in the illustrated embodiment) is then fed through the line 11 to a hydrogen separator 6 where it is separated into a hydrogen-rich gas (first gas mixture) and a methane- and/or ethane rich gas (second gas mixture) which are discharged from the separator 6 through lines 12 and 13, respectively.

The separation of hydrogen may be effected by any known method such as a method using a separation membrane or a cryogenic separation method. From the standpoint of selective hydrogen separation efficiency, the use of the membrane method is preferred. From the standpoint of aromatics yield, on the other hand, the cryogenic separation method is preferred since the off gas, which is obtained in this method and which is to be recycled to the catalytic conversion step, contains a higher unreacted propane content as compared with that obtained in the membrane method. The membranes to be used in the hydrogen separation method may be formed of, for example, a polyimide, a polysulfone and a blend of polysulfone and a polydimethylsiloxane. If desired, an additional membrane separator or a pressure swing adsorption separator may be disposed downstream of the membrane separation method so as to recover hydrogen with an improved purity.

The methane- and/or ethane-rich gas is discharged from the hydrogen separator 6 through a line 13 and at least a portion thereof is recycled through a line 17 into the catalytic conversion zone 1 as described previously. A portion of the methane- and/or ethane-rich gas may be discharged out of the system through a line 14 so as to maintain the amount of the recycled gas in a predetermined range.

The liquid phase (third liquid phase) obtained in the separation zone (high pressure separation tower 4, in the illustrated embodiment) is fed through the line 10 to a stabilizer (distillation tower) 5 and is separated there into an aromatic hydrocarbon-containing product and a light hydrocarbon-containing gas. The product is discharged as a bottom fraction from the stabilizer, cooled by indirect heat exchange with the liquid phase supplied through the line 10 and recovered through a line 16. The light hydrocarbon-containing gas topped from the stabilizer and containing C₃ and C₄ hydrocarbons as a major component is discharged through a line 15 and is recycled, together with the above methane- and/or ethane-rich gas, through the line 17 as the previously-described recycle gas.

The recycling of methane and/or ethane give the following advantages:

1. Since the catalytic aromatization reaction by dehydrogenative cyclization is endothermic, lowering of the temperature of the catalyst layer is disadvantageous in the aromatization. Methane and ethane are not aromatized under the reaction conditions and, thus, may be regarded as being an inert gas. By recycling heated methane and/or ethane to the reaction zone, the recycle gas serves to function as a heating medium for heating the catalyst layer, so that the lowering of the catalyst temperature can be prevented to permit the aromatization reaction to proceed favorably with an improved aromatics yield.
2. The recycling can lower the hydrogen partial pressure in the reaction zone. Since the aromatization produces hydrogen, the lowering of the hydrogen partial pressure is favorable for improving aromatics yield.
3. The recycling can increase the gas flow rate (gas hourly space velocity) so that the period of time for which the reactants are contacted with the active sites of the catalyst can be reduced, thereby to avoid the occurrence of excessive reactions resulting in the formation of coke. As a consequence, the catalyst inactivation with time can be prevented and, hence, the aromatics yield can be improved.

According to the process of the present invention, paraffins and/or olefins having 2-7 carbons can be converted into aromatic hydrocarbons with a predetermined range of high aromatics yields so that the process can be performed with a high efficiency in a stable manner. Further, since the catalytic conversion is performed while increasing the reaction temperature and since the discharge of methane and/or ethane, which are produced as by-product in the catalytic conversion step, out of the system is maintained at a minimum level, the aromatics yield can be controlled within a high range.

The following examples will further illustrate the present invention. Parts are by weight.

Example 1

Butane (specific gravity: 0.576) is converted into aromatic hydrocarbons in an amount of 10000 barrel per day using a conversion system as shown in the FIGURE. Thus, 100 parts/hour of butane is fed through the line 7 and mixed with about 72 parts/hour of a recycle gas supplied from the line 17. The mixture is heated to about 470 °C by indirect heat exchange with a product stream discharged from the conversion zone 1 and then to about 570 °C by a heater and introduced through the line 18 into the conversion zone 1 containing an aluminogallosilicate catalyst. The mixture is thus subjected to catalytic aromatization.

The product stream discharged from the last reactor of the conversion zone 1 had a temperature of about 550° C and a pressure of about 3 kg/cm²G. The product stream is cooled by indirect heat exchange with the raw material mixture as mentioned above and further cooled in another heat exchanger to about 40 °C. The cooled product stream is fed to the low pressure separator 2. A first gas phase is discharged through the line 19 from the low pressure separator 2 and, after being pressurized, is fed to the middle pressure separator 3. A second liquid phase is discharged through the line 21 and recycled to the low pressure separator 2, while a second gas phase is discharged through the line 20 and is further pressurized. The pressures at the tops of the low and middle pressure separators 2 and 3 are about 2 and about 7 kg/cm²G, respectively. The first liquid phase discharged from the low pressure separator through the line 9 is pressurized and mixed with the pressurized second gas phase and the mixture at about 40 °C is fed to the high pressure separator 4, where it is separated into a third gas phase discharged through the line 11 with a flow rate of about 112 parts/hour and a third liquid phase discharged through the line 10 with a flow rate of about 60 parts/hour.

The third liquid phase is heated to about 150 °C by indirect heat exchange with an aromatic hydrocarbon product stream supplied from the stabilizer 5 at about 270 °C and is introduced into the stabilizer 5. From the stabilizer, 2 parts/hour of a light hydrocarbon gas containing methane, ethane, propane and butane is discharged through the line 15 and about 58 parts/hour of the aromatic hydrocarbon product stream is discharged through the line 16. The product feed at about 270 °C is cooled to about 180 °C by the heat exchange with the third liquid phase supplied through the line 10. The product feed contained benzene, toluene and xylene as a major component thereof.

The third gas phase is fed to the hydrogen separator 6 of a membrane type at about 85 °C. About 12 parts/hour of a hydrogen-rich gas is discharged through the line 12. The hydrogen-rich gas contained about 4 parts/hour of hydrogen and balance being essentially methane, ethane, propane and butane. A methane-rich gas is discharged from the hydrogen separator 6 through the line 13. A portion of the methane-rich gas is diverted through the line 14. The remainder of the methane-rich gas is joined with the light hydrocarbon gas discharged from the stabilizer through the line 15 and the resulting mixture is recycled through the line 17 at a rate of about 72 parts/hour to the line 18.

The above process is continued for 2 days while intermittently increasing the reaction temperature in the reaction zone 1. Thus, the reaction is started at a temperature of 562 °C and terminated at a temperature of 571 °C. The reaction zone 1 is composed of two series of packed bed reactors, with each series consisting of 4 reactors. While one of the two series of reactors are used for effecting the catalytic conversion, the other series of reactors are subjected to a regeneration treatment. After 2 the days reaction, valves are switched so that the catalytic conversion is performed using the other series of reactors containing regenerated catalyst, with the catalyst of the one series of reactors being subjected to regeneration. The whole of the process is, therefore, carried out continuously. In each 2 days reaction, the conversion temperature is stepwisely increased.

Example 2

Using a system similar to that used in Example 1, light naphtha is subjected to a catalytic conversion. The catalyst used is composed of alumina (binder) and a crystalline aluminogallosilicate having a particle size in the range of 0.1-10 µm, 80 % by weight of the crystalline aluminogallosilicate having a particle size in the range of 1-4 µm. The crystalline aluminogallosilicate had a SiO₂/Ga₂O₃ molar ratio of 186.8, a SiO₂/(Al₂O₃ + Ga₂O₃) molar ratio of 48.7 and a SiO₂/Al₂O₃ molar ratio of 65.9. The conversion is continuously performed at a pressure of 3 kg/cm²G for about 6 months. The compositions of the streams passing through the line 7 (naphtha raw material feed), line 17 (recycle gas stream), line 18 (mixture feed), line 8 (conversion product stream), line 12 (hydrogen-rich gas stream) and line 16 (aromatic hydrocarbon product stream) are as summarized in Tables 1-4.

Table 1 shows the results after 1 hour from the commencement of the conversion using the fresh catalyst, Table 2 shows the results after 24 hours from the commencement of the conversion using the fresh catalyst. The temperature at which the reaction using the fresh catalyst is performed is increased by 12 °C from the commencement to the end of the 24 hours reaction so as to maintain the aromatics yield at about 59 %. The reaction

temperature after 1 hour from the commencement of the reaction is about 495 °C.

Table 3 shows the results after 1 hour from the commencement of the conversion using a freshly regenerated catalyst obtained by regenerating the catalyst used for 6 months with repeated regeneration treatments, and Table 4 shows the results after 24 hours from the commencement of the conversion using the above-mentioned regenerated catalyst. The temperature at which the reaction using the regenerated catalyst is performed is increased by 10 °C from the commencement to the end of the 24 hours reaction so as to maintain the aromatics yield at 51 %. The reaction temperature after 1 hour from the commencement of the reaction is about 515 °C.

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Table 1

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas * (line 12) (line 14)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	5.7	5.7	29.7	24.0	0
Methane	0	399.6	399.6	566.1	166.5	0
Ethane	0	371.7	371.7	510.4	138.7	0
Propane	0	86.6	86.6	115.2	28.6	0
Butane	4.4	4.9	9.3	6.3	1.4	0
Pentane	450.4	0.4	450.8	0.4	0	0
Paraffins (C ₆ +) (C ₂ +) Olefins	397.3	0	397.3	0	0	0
Benzene	14.5	8.9	9.4	12.2	3.3	0
Toluene	2.9	16.2	30.7	161.2	9.3	135.7
Xylene	0	7.4	10.3	214.0	4.4	202.2
Aromatics (C ₉ +) Aromatics	0	1.2	1.2	89.3	0.7	87.4
	0	0.1	0.1	67.9	0	67.8
Flow Rate of Stream (kg/H)	870.0	902.7	1772.7	1772.7	376.9	493.1
Aromatics Yield (%)	-	-	-	-	-	59.5

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Table 2

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas * (line 12) (line 14)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	6.2	6.2	32.2	26.0	0
Methane	0	342.6	342.6	485.1	142.5	0
Ethane	0	325.0	325.0	445.5	120.5	0
Propane	0	194.1	194.1	256.9	62.8	0
Butane	4.4	13.8	18.2	17.4	3.6	0
Pentane	450.4	0.4	450.8	0.9	0.1	0.4
Paraffins (C ₆ +) Olefins (C ₂ +) Benzene Toluene Xylene Aromatics (C ₉ +) Flow Rate of Stream (kg/H)	397.3 0.5 14.5 2.9 0 0	0 20.1 12.0 6.9 1.4 0.1	397.3 20.6 26.5 9.8 1.4 0.1	0 28.5 132.3 216.4 110.2 67.2	0 7.1 7.1 4.1 0.8 0	0 1.3 113.2 205.4 108.0 67.1
Aromatics Yield (%)	-	-	-	-	-	59.3

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Table 3

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas * (line 12)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	5.7	5.7	30.2	24.5	0
Methane	0	271.3	271.3	388.7	117.4	0
Ethane	0	264.0	264.0	365.0	101.0	0
Propane	0	326.7	326.7	433.4	106.7	0
Butane	4.4	27.5	31.9	52.5	10.3	14.7
Pentane	450.4	5.2	455.6	16.0	1.7	9.1
Paraffins (C ₆ +))	397.3	0	397.3	0.2	0	0.2
Olefins (C ₂ +))	0.5	33.1	33.6	50.7	12.2	5.4
Benzene	14.5	8.9	23.4	108.8	5.5	94.4
Toluene	2.9	5.6	8.5	198.1	3.4	189.1
Xylene	0	1.2	1.2	113.7	0.8	111.7
Aromatics (C ₉ +))	0	0.1	0.1	62.0	0	61.9
Flow Rate of Stream (kg/H)	870.0	949.3	1819.3	1819.3	383.5	486.5
Aromatics Yield (%)	-	-	-	-	-	54.8

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Table 4

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas * (line 12) (line 14)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	5.6	5.6	30.1	24.5	0
Methane	0	209.2	209.2	302.5	93.3	0
Ethane	0	199.7	199.7	277.5	77.8	0
Propane	0	460.9	460.9	609.6	148.7	0
Butane	4.4	46.6	51.0	90.5	16.9	27.0
Pentane	450.4	4.3	454.7	15.3	1.4	9.6
Paraffins (C ₆ +))	397.3	0.1	397.4	0.5	0	0.4
Olefins (C ₂ +))	0.5	61.8	62.3	94.2	22.5	9.9
Benzene	14.5	7.1	21.6	96.8	4.3	85.4
Toluene	2.9	4.5	7.4	183.8	2.8	176.5
Xylene	0	1.0	1.0	113.3	0.7	111.6
Aromatics (C ₉ +))	0	0.1	0.1	56.8	0	56.7
Flow Rate of Stream (kg/H)	870.0	1000.9	1870.9	1870.9	392.9	477.1
Aromatics Yield (%)	-	-	-	-	-	51.3

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Example 3

Example 2 is repeated in the same manner as described except that butane is used as raw material feed in place of the light naphtha. The results are summarized in Tables 5 and 6. Table 5 shows the results after 1 hour from the commencement of the conversion using the fresh catalyst, and Table 6 shows the results after 47.5 hours from the commencement of the conversion using a freshly regenerated catalyst obtained by regenerating the catalyst used for 6 months with repeated regeneration treatments.

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Table 5

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas (line 12) (line 14)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	7.1	7.1	38.1	31.0	0
Methane	0	445.4	445.4	653.8	208.4	0
Ethane	0	432.6	432.6	615.3	182.7	0
Propane	16.0	106.7	122.7	147.0	40.3	0
Butane	984.0	6.2	990.2	8.1	1.9	0
Pentane	0	0.2	0.2	0.2	0	0
Paraffins (C ₆ +) Olefins (C ₂ +) Benzene Toluene Xylene	0	0	0	0	0	0
	0	9.7	9.7	13.6	3.9	0
	0	17.4	17.4	158.7	10.9	130.4
	0	8.8	8.8	230.3	5.8	215.7
	0	1.4	1.4	96.6	0.9	94.2
Aromatics (C ₉ +) Flow Rate of Stream (kg/H)	0	0.1	0.1	74.0	0	73.9
	1000.0	1035.6	2035.6	2035.6	485.8	514.2
Aromatics Yield (%)	-	-	-	-	-	53.2

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Table 6

Stream	Naphtha Raw Feed (line 7)	Recycle Gas (line 17)	Mixture Feed (line 18)	Conversion Product (line 8)	H ₂ and Off Gas * (line 12) (line 14)	Aromatic HC Product (line 16)
Composition (kg/H)						
Hydrogen	0	6.9	6.9	38.9	31.9	0
Methane	0	222.8	222.8	336.7	113.9	0
Ethane	0	220.3	220.3	319.9	99.6	0
Propane	16.0	558.2	574.2	770.8	212.6	0
Butane	984.0	55.0	1039.0	107.3	23.3	29.0
Pentane	0	3.0	3.0	10.4	1.2	6.2
Paraffins (C ₆ +) Olefins (C ₂ +) Benzene	0	0.1	0.1	0.5	0	0.4
Toluene	0	61.7	61.7	96.9	26.2	9.0
Xylene	0	6.8	6.8	86.0	4.8	74.4
Aromatics (C ₉ +) Flow Rate of Stream (kg/H)	0	5.2	5.2	193.2	3.7	184.3
Aromatics Yield (%)	0	1.3	1.3	120.9	0.9	118.7
		0	0	59.8	0	59.8
	1000.0	1141.3	2141.3	2141.3	518.2	481.8
	-	-	-	-	-	44.7

*: Total of H₂-rich gas from line 12 and off-gas from line 14

Example 4

Using a system similar to that used in Example 1, light naphtha was subjected to a catalytic conversion. The catalyst used was composed of alumina (binder) and an acid type, activated crystalline aluminogallosilicate having a particle size of in the range of 0.1-10 μm and a $\text{SiO}_2/\text{Ga}_2\text{O}_3$ molar ratio of 158.9, a $\text{SiO}_2 (\text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3)$ molar ratio of 46.1 and a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 64.8. The aluminogallosilicate had a particle size in the range of 0.1-3.5 μm in 80 % of its weight. The catalyst was packed in two series of conversion reactors, with each series consisting of two reactors. The two series of reactors were used alternately for conversion and regeneration to perform continuous catalytic conversion. The operations were switched at a cycle of 2-3 days. The conversion was performed while intermittently increasing the reaction temperature in the inlet of the catalyst layer as shown in Table 8 at a pressure in the outlet of the reactor of 3 $\text{kg}/\text{cm}^2\text{G}$ and a raw material feed rate of 860 kg/hour with a recycle ratio (by weight) of the recycle gas to the raw material feed of 1.3. A commercially available membrane-type separator was used for the separation of hydrogen-rich gas. The aromatics yields at various process time are shown in Table 8.

Table 8

Process Time (hours after start of the feed of the raw material)	6.5	14.5	21.5	24.5	30.5	45.5
Temperature in the Inlet of the Catalyst Layer ($^{\circ}\text{C}$)	526	526	531	536	545	545
Aromatics Yield (% by weight)	48.2	46.4	45.6	48.2	50.4	50.2

Claims

1. A process for the production of aromatic hydrocarbons from an aliphatic hydrocarbon having 2-7 carbon atoms, said process comprising the steps of:
 - (a) mixing a feed of an aliphatic hydrocarbon having 2-7 carbon atoms with a recycle gas to obtain a first mixture;
 - (b) contacting said first mixture with an aluminogallosilicate catalyst to convert the aliphatic hydrocarbon into aromatic hydrocarbons and to obtain a second mixture containing the aromatic hydrocarbons;
 - (c) separating said second mixture into a gas phase and a liquid phase containing aromatic hydrocarbons;
 - (d) separating said gas phase into a first gas mixture rich in hydrogen and a second gas mixture rich in methane and/or ethane;
 - (e) separating said liquid phase into an aromatic hydrocarbon-containing product and a light hydrocarbon-containing gas; and
 - (f) recycling at least part of said second gas mixture and said light hydrocarbon-containing gas to step (a) as said recycle gas, the temperature at which said first mixture is contacted with said catalyst is increased with time to maintain the aromatics yield R within the range of 40-75 %, wherein R is defined as follows:

$$R = A/B \times 100 (\%)$$

where A is the weight of the aromatic hydrocarbons contained in said second mixture and B is the weight

of the aliphatic hydrocarbons which has 2-7 carbon atoms, which are contained in said aliphatic hydrocarbon feed and which are other than ethane.

- 5 2. A process as claimed in claim 1, wherein a portion of the second gas mixture is discharged out of the process.
3. A process as claimed in claim 1, wherein step (c) is performed using two or more gas-liquid separators operated at different pressures.
- 10 4. A process as claimed in claim 1, wherein the amount of said recycle gas is 0.5-3 parts by weight per part by weight of said aliphatic hydrocarbon feed.
- 15 5. A process as claimed in claim 1, wherein said aluminogallosilicate catalyst is a crystalline aluminogallosilicate having a particle size in the range of about 0.05-20 μm , at least 80 % by weight of said crystalline aluminogallosilicate having a particle size in the range of 0.1-10 μm , said crystalline aluminogallosilicate containing about 0.1-2.5 % by weight of aluminum and about 0.1-5 % by weight of gallium in the skeleton thereof.

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