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OPENING OF NAPHTHENE RINGS**(75) Inventors: **Vincenzo Calemma**, San Donato
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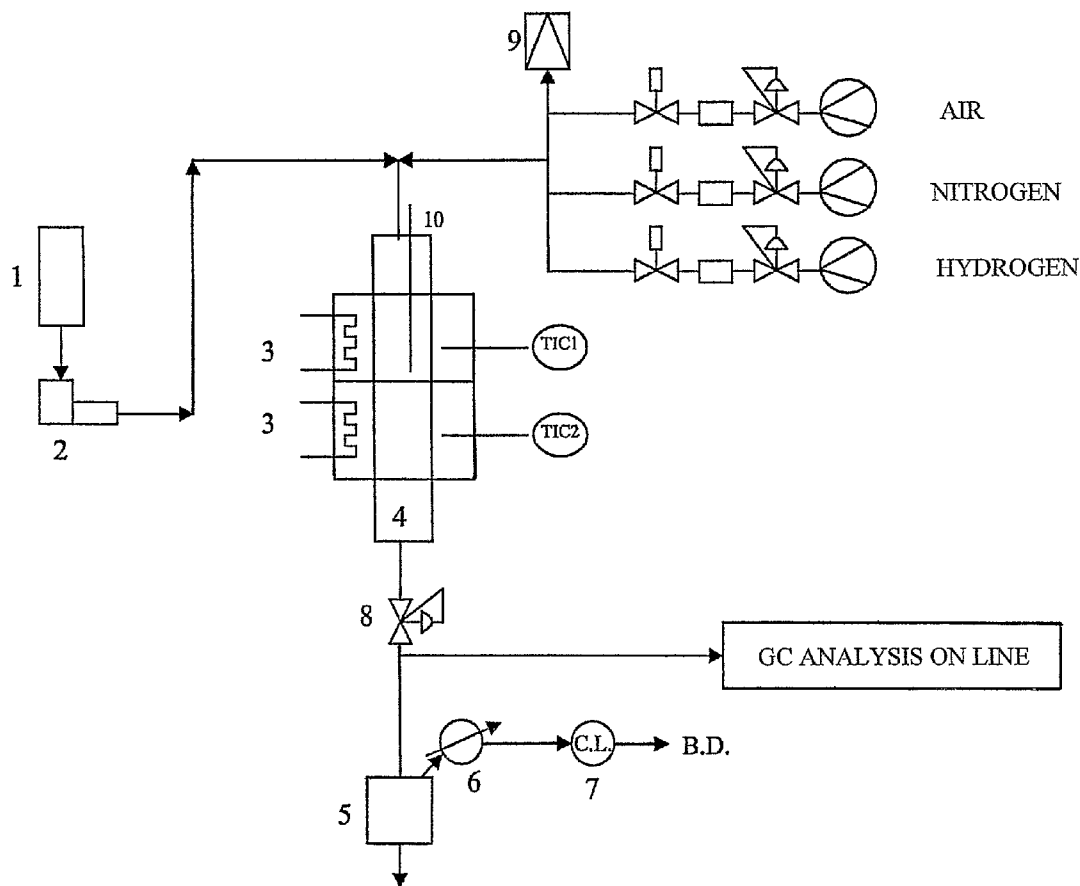
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Publication Classification(51) **Int. Cl.****C10G 45/64** (2006.01)(52) **U.S. Cl.** **208/138; 502/66**(57) **ABSTRACT**

A process is described for the upgrading of distillates having a boiling point ranging from 100 to 450° C., which comprises the opening of the ring of the naphthene compounds contained in these distillates to obtain paraffinic compounds, rich in branched paraffins, having for the most part the same number of carbon atoms as the starting naphthene. The process is carried out in the presence of a bifunctional catalytic system comprising one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re, and a silico-aluminate of an acidic nature, selected from a micromesoporous silico-alumina and a zeolite belonging to the MTW group.



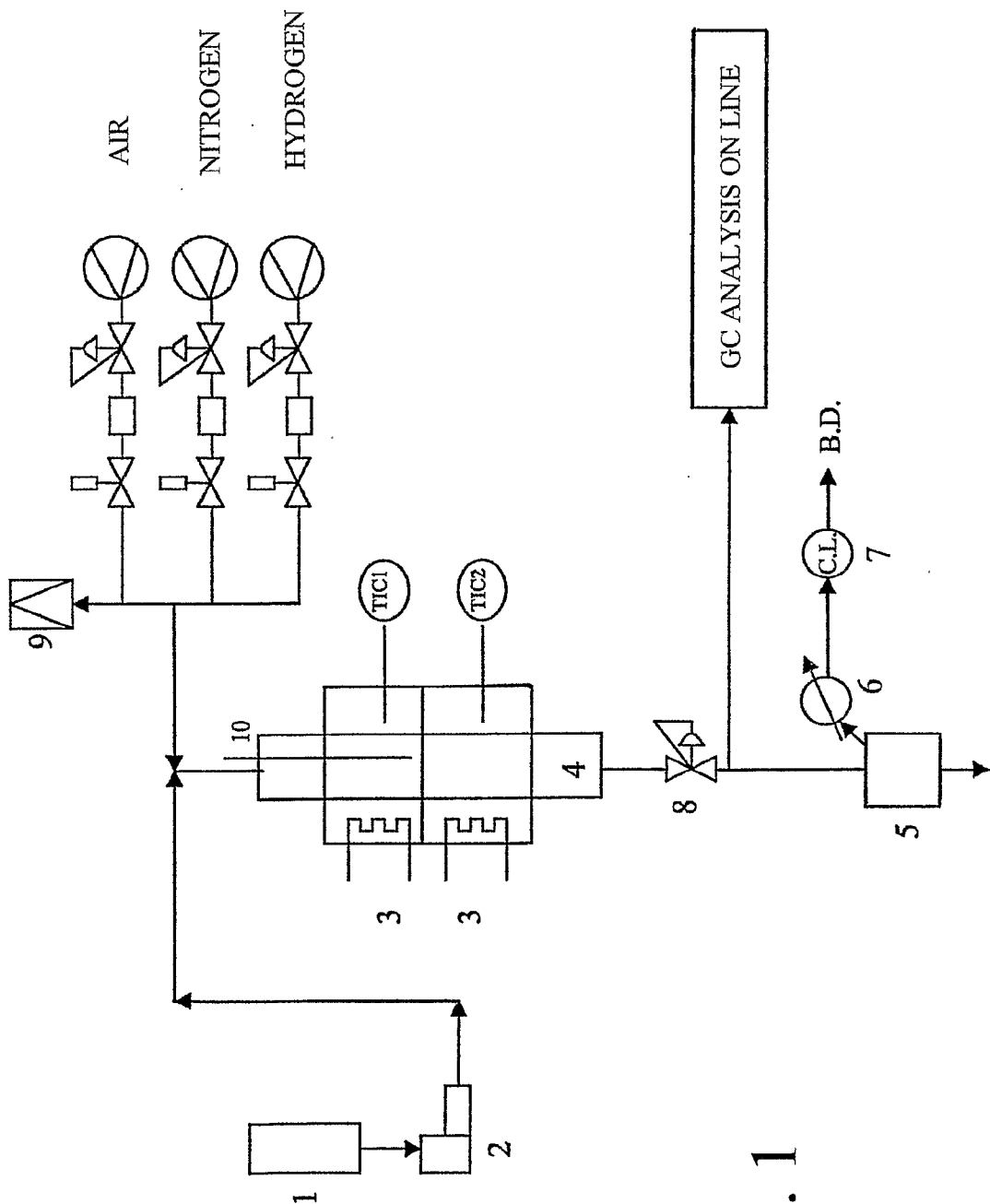


Fig. 1

PROCESS AND CATALYSTS FOR THE OPENING OF NAPHTHENE RINGS

[0001] The present invention relates to a process for the upgrading of distillates having a boiling point ranging from 100 to 450° C. The process comprises the opening of the ring of the naphthene compounds contained in these distillates to obtain prevalently branched, open-chain paraffinic compounds, mainly having the same number of carbon atoms as the starting naphthene.

[0002] The process is carried out in the presence of a bifunctional catalytic system comprising one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re, and a silico-aluminate of an acidic nature, selected from a micro-mesoporous silico-alumina having a suitable composition, and a zeolite belonging to the MTW group.

[0003] The present invention also relates to particular catalytic compositions. The production of clean fuels for use in new generation engines which reduce exhaust emissions, is one of the main problems of the refining industry.

[0004] The definition of future specifications of fuels is still subject to discussion, however in order to meet with the increasingly strict regulations with respect to emissions, medium distillates will undoubtedly be requested with significantly different characteristics from those currently used, also from the point of view of composition.

[0005] As far as gas oil for motor vehicles is concerned, in addition to a reduction in the sulfur content, other important aspects linked to the quality of diesel fuel and which will probably be the object of stricter regulations in the near future, are: the content of aromatic products, the density, the T95 (temperature at which 95% of the product distills) and the cetane number.

[0006] Most probably, not all of the characteristics listed above will be the object of future regulations, it is certain however that from a compositional point of view, the reduction in the content of aromatic products by saturation of the ring to naphthene compounds represents an effective method for improving the properties of diesel fuel, as it leads to a reduction in the density, the boiling point with the same molecular weight and an increase in the cetane number. A further improvement in the characteristics in the above sense, can be obtained through the opening reaction of the naphthene ring to open-chain aliphatic compounds. Paraffins are the best compounds as, with the same molecular weight, they have a higher cetane number, a lower density and boiling point.

[0007] Generally speaking, there are two processes commercially available for obtaining medium distillates with a reduced content of aromatic products: dearomatization and hydrocracking.

[0008] In the former case, the conversion of the aromatic structures into naphthene structures causes a significant reduction in the density and the boiling point, and an increase in the cetane number with low yields to cracking products. It should be noted, however, that in this case there is a high hydrogen consumption, with rather limited increases in the cetane number and reduction in the density.

[0009] A typical process for the production of distillates is hydrocracking. The catalysts used are of the bifunctional type, i.e. consisting of metals which have a hydro-dehydro-

genating function, supported on a phase which can have various acidity characteristics, generally containing zeolite. Under the typical operating conditions, there is a significant reduction in the content of aromatic rings, but with much high yields to light products.

[0010] A method which has been quite recently proposed for considerably improving the characteristics of medium distillates, envisages saturation of the aromatic rings followed by the selective opening of the naphthene ring into the corresponding aliphatic chains with the minimum possible loss of carbon into lighter products. In this case, in the ideal situation in which all the aromatic structures are transformed into open-chain aliphatic compounds, there would be a product essentially consisting of a mixture of iso and normal paraffins, thus obtaining the maximum benefit in terms of density, boiling point and cetane number. Whereas the hydrogenation of aromatic structures is a relatively simple operation, and there are various catalysts commercially available, the selective opening of the naphthene ring is, on the other hand, much more complex. Generally speaking, the opening of the naphthene ring can be effected according to two mechanisms:

[0011] breakage of the C—C bond by means of a mechanism of the carbo-cationic type; this mechanism, operating with classical bifunctional catalysts consisting of a metal which has a hydro/dehydrogenating function on an acidic support, is generally characterized by a low selectivity, due to the presence of dealkylation reactions and the secondary cracking of the alkanes formed;

[0012] breakage of the C—C bond of the ring via hydrogenolysis, catalyzed by a metal such as platinum, rhodium or iridium, on a non-acidic support. One of the characteristics of this mechanism is that the conversion of rings with six chain-ends is much slower and less selective with respect to rings with five chain-ends.

[0013] In the case of the naphtha cut, there are various processes in which the charge is upgraded by means of the hydro-decyclization of the naphthene compounds. These processes are characterized in that they are carried out in two steps: in the first step, the opening of the naphthene ring is obtained, and in the second step the paraffins formed are isomerized in order to increase the octane number.

[0014] U.S. Pat. No. 5,463,155, for example, describes a combined process for increasing the content of isoparaffins in naphtha, which comprises:

[0015] a treatment step of naphtha, giving a paraffin-enriched intermediate mixture, effected with a non-acidic catalyst comprising at least one metal of the platinum group and a support selected from metal oxides and large-pore zeolites, wherein the support is made non-acidic by means of suitable impregnation or ion exchange treatment with solutions of alkaline or alkaline-earth salts;

[0016] a second step in which the mixture thus obtained is subjected to isomerization in the presence of an acid catalyst containing at least one metal of the platinum group.

[0017] U.S. Pat. No. 5,382,731 describes a two-step process in which the charge is put in contact, in the first reactor,

with a ring-opening catalyst, consisting of a component which has a hydro-dehydrogenating function and an acidic solid consisting of zirconia modified with tungstate. The second reactor operates in such a way as to favour isomerization. In this case, the catalyst consists of platinum deposited on alumina and the reaction takes place in the presence of a chlorinated compound. U.S. Pat. No. 5,763,731 describes a process for selective ring-opening in compounds of the naphthene type, giving paraffinic-type compounds. The process uses catalysts containing a metal selected from Ir, Ru or their mixtures and is capable of reducing the number of cyclic structures in the product by the opening of the ring, without dealkylation of the alkyl substituents linked to these cycles. As the end-product has an increased cetane number, the paraffins thus obtained prove to be mainly linear or with low branchings. This patent also specifies that the use of platinum on a Y-type zeolitic support leads to very low selectivities towards the opening of the ring.

[0018] EP 875288 describes a process for the ring-opening of organic compounds containing cycles using a catalyst containing a support selected from alumina, silica, zirconia or their mixtures, a metal selected from Pt, Pd, Rh, Re, Ir, Ni, cobalt and their mixtures, and a metal selected from W, Mo, La and rare earth metals. The product obtained mainly contains n-paraffins, whereas skeleton isomerization, cracking and dehydrogenation reactions are substantially suppressed.

[0019] When the reaction is effected on bifunctional catalysts, the splitting of the C—C bond present in paraffinic chains or naphthene compounds takes place by the formation of a carbo-cation and subsequent β -splitting reaction. The most important difference between paraffinic and naphthene compounds is the splitting rate of the C—C bond which, in the case of naphthene compounds is lower in orders of magnitude (Weitkamp, J. and Ernst, S., Catal. Today 19, 107 (1994)). As a result of this difference in reactivity, the subsequent cracking reactions of the products formed, cause an extremely low selectivity towards the opening of the naphthene ring.

[0020] The patent EP 582347 describes a bifunctional catalyst which comprises:

[0021] a) a component of an acidic nature consisting of a gel of silica and alumina amorphous to X-rays, having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 30 to 500, a surface area ranging from 500 to 1,000 m^2/g , with a porosity of 0.3 to 0.6 mg/g , a pore diameter prevalently within the range of 10-30 Å;

b) one or more metals belonging to group VIII.

[0022] This material is capable of catalyzing the hydro-isomerization of n-paraffins.

[0023] The Applicant has now surprisingly found a process for obtaining the opening of the naphthene rings to give paraffinic compounds, preferably branched, in a single reaction step, with high conversions and selectivities, using catalytic compositions having suitably calibrated acidity characteristics. Contrary to what is currently known, it has been found that by the appropriate selection of the acidic component and metal, it is possible to obtain, also in the case of a bifunctional catalyst, conversions of naphthene rings to paraffins with significantly higher selectivities with respect to the known art.

[0024] A first object of the present invention therefore relates to a process for the upgrading of distillates having a boiling point ranging from 100 to 450° C., by the ring opening of the naphthene compounds contained in the distillates to give paraffin mixtures, said process consisting in treating said distillates, in the presence of hydrogen, with a catalytic system comprising:

a) one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re

[0025] b) a silico-aluminate of an acidic nature selected from a zeolite belonging to the MTW group and a completely amorphous, micro-mesoporous silico-alumina, having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 30 to 500, a surface area greater than 500 m^2/g , a pore volume within the range of 0.3-1.3 ml/g , an average pore diameter of less than 40 Å.

[0026] The distillates thus treated prove to be enriched in paraffins mainly having the same number of carbon atoms as the starting naphthenes.

[0027] Isoparaffinic compounds prevail in the paraffinic mixtures thus obtained.

[0028] The acid component (b) of the catalytic composition can be selected from zeolites of the MTW type: the MTW group is described in Atlas of zeolite structure types, W. M. Meier and D. H. Olson, 1987, Butterworths. ZSM-12 zeolite, described in U.S. Pat. No. 3,832,449, is preferably used for the process of the present invention.

[0029] When the component of an acidic nature (b) is a silico-alumina, a preferred aspect is that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranges from 50/1 to 300/1 and the porosity from 0.4 to 0.5 ml/g .

[0030] Micro-mesoporous, completely amorphous silico-aluminas, useful for the present invention, called MSA, are described in U.S. Pat. No. 5,049,536, EP 659,478, EP 812,804. Their XRD spectrum from powders does not have a crystalline structure and does not show any peak.

[0031] Catalytic compositions which can be used in the present invention, in which the acid component is a silico-alumina of the MSA type, are described in EP 582,347.

[0032] As far as the metallic component of the catalytic compositions used in the process of the present invention are concerned, this is selected from Pt, Pd, Ir, Ru, Rh, Re and their mixtures. According to a particularly preferred aspect of the present invention, the metal is platinum, iridium or their mixtures.

[0033] The metal or mixture of metals is preferably in a quantity ranging from 0.1 to 5% by weight with respect to the total weight of the catalytic composition, and preferably ranges from 0.3 to 1.5%.

[0034] The weight percentage of the metal, or metals, refers to the content of metal expressed as a metallic element; in the end-catalyst, after calcination, said metal is in the form of an oxide.

[0035] The catalytic compositions containing one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re, and, as acidic component completely amorphous micro-mesoporous silico-aluminas of the MSA type, are new and are a particular aspect of the present invention.

[0036] Before being used, the catalyst is activated by means of the known techniques, for example by means of a reduction treatment, and preferably by drying and subsequent reduction. The drying is effected in an inert atmosphere at temperatures ranging from 25 to 100° C., whereas the reduction is obtained by thermal treatment of the catalyst in a reducing atmosphere (H₂) at a temperature ranging from 300 to 450° C.

[0037] The acidic component (b) of the catalyst adopted in the process of the present invention can be used as such or in extruded form with traditional binders, such as for example aluminum oxide, bohemite or pseudo-bohemite. The acidic component (b) and the binder can be premixed in weight ratios ranging from 30:70 to 90:10, preferably from 50:50 to 70:30. At the end of the mixing, the product obtained is consolidated in the desired end-form, for example in the form of extruded pellets or tablets.

[0038] With respect to the metal phase (a) of the catalyst, this can be introduced by means of impregnation or ion exchange. According to the first technique, the acidic component (b), also in extruded form, is wetted with an aqueous solution of a compound of the metal, operating, for example, at room temperature, and at a pH ranging from 1 to 4. The aqueous solution preferably has a concentration of the metal expressed as g/l ranging from 0.2 to 2.0. The resulting product is dried, preferably in air, at room temperature, and is calcined in an oxidizing atmosphere at a temperature ranging from 200 to 600° C.

[0039] In the case of alcohol impregnation, the acidic component (b) is suspended in an alcohol solution containing the metal. After impregnation, the solid is dried and calcined.

[0040] According to the ion exchange technique, the acidic component (b) is suspended in an aqueous solution of a complex or salt of the metal, operating at room temperature and at a pH ranging from 6 to 10. After the ion exchange, the solid is separated, washed with water, dried and finally thermally treated in an inert or oxidizing atmosphere. Temperatures useful for the purpose range from 200 to 600° C.

[0041] Metal compounds well suited for the preparations described above are: H₂PtCl₆, Pt(NH₃)₄(OH)₂, Pt(NH₃)₄Cl₂, Pd(NH₃)₄(OH)₂, PdCl₂, H₂IrCl₆, RuCl₃, RhCl₃. When the catalytic composition comprises more than one metal, the impregnation is carried out as follows: the acidic component (b), also in extruded form, is wetted with a solution of a compound of a first metal, the resulting product is dried, optionally calcined, and is impregnated with a solution of a compound of a second metal. The product is dried and calcination is then effected in an oxidizing atmosphere at a temperature ranging from 200 to 600° C. Alternatively, a single aqueous solution containing two or more compounds of different metals can be used for contemporaneously introducing said metals.

[0042] The catalytic compositions of the present invention in which the acidic component is a silico-alumina of the MSA type with a pore volume greater than 0.6 ml/g, are new and are a further object of the present invention.

[0043] The catalytic compositions of the present invention in which the acidic component is of the ZSM-12 type, are new and are a further aspect of the present invention.

[0044] The distillates which can be subjected to this upgrading process are mixtures having boiling points within the range of 100 to 450° C. In particular, they can be hydrocarbon cuts selected from naphthas, diesel, kerosene, jet fuel, light cycle oil, HVGO, heavy FCC fraction.

[0045] The process of the present invention is carried out at a temperature ranging from 240 to 380° C., at a pressure ranging from 20 to 70 atm, at a WHSV ranging from 0.5 to 2 hours⁻¹ and a ratio between hydrogen and charge (H₂/HC) ranging from 400 to 2,000 Nlt/kg. It is preferable to operate at a pressure higher than 40 atm and lower than or equal to 70 atm, whereas the temperature preferably ranges from 240 to 320° C. when the acidic component ((b) is a zeolite of the MTW type, whereas it preferably ranges from 300 to 380° C. when the acidic component (b) is a silico-alumina.

[0046] The following experimental examples are provided for a better illustration of the present invention.

EXAMPLE 1

Preparation of Catalyst A

ZSM-12/0.5% Pt

[0047] a) Preparation of ZSM-12 Zeolite

[0048] 127 grams of tetra-ethyl ammonium hydroxide at 40% by weight, in aqueous solution, are added to 24 grams of demineralized water. 4 grams of sodium aluminate at 56% by weight of Al₂O₃ are then added. The limpid solution thus obtained is poured, under stirring, into 350 grams of Ludox HS 400 colloidal silica. After brief stirring, a homogeneous limpid gel is obtained, which is poured into a 1 litre autoclave made of AISI 316 steel, equipped with an anchor stirrer. The gel is left to crystallize under hydro-thermal conditions at 160° C. for 60 hours. At the end of this phase, the autoclave is cooled to room temperature. The slurry obtained is homogeneous with a milky appearance. The slurry is centrifuged. The solid discharged is washed by redispersion in water, centrifuged again, dried at 120° C. and calcined at 550° C. for 5 hours. Upon X-ray diffraction analysis, the solid obtained proves to consist of pure ZSM-12. The solid obtained is subsequently exchanged in ammonia form by treatment with a 3 M solution of ammonium acetate. Upon subsequent calcination at 550° C. for 5 hours, the zeolite is obtained in acidic form.

[0049] b) Deposition of Platinum (0.5% by Weight of Pt)

[0050] In order to disperse the platinum onto the zeolite prepared in the previous step (a), an aqueous solution of hexachloroplatinic acid (H₂PtCl₆), hydrochloric acid and acetic acid was used, in the following molar ratios: H₂PtCl₆/HCL/CH₃COOH=1/0.84/0.05, having a platinum concentration of 0.75 g/l. A volume of 200 ml of this solution was added to 30 g of the zeolite prepared as described above, so that all the solid was covered by the solution, to avoid heterogeneity in the platinum distribution. The suspension thus obtained was maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent was subsequently removed by heating to about 70° C. under vacuum. The dry product was finally calcined under a stream of air with the following temperature profile 25-350° C. in two hours, 360° C. for 3 hours.

[0051] A ZSM-12 zeolite is obtained, containing 0.5% by weight of platinum.

EXAMPLE 2

Preparation of Catalyst B

ZSM-12/1% Pt

[0052] A quantity of platinum equal to 1% by weight, is deposited on a ZSM-12 zeolite, prepared as described in step (a) of the previous example 1. The same procedure described in step (b) of Example 1 is adopted for the deposition, using 400 ml of the same aqueous solution of hexachloroplatinic acid and 30 g of ZSM-12 zeolite.

At the end, a ZSM-12 zeolite is obtained, containing 1% of platinum.

EXAMPLE 3

Preparation of Catalyst C

ZSM-12/1% Pt

[0053] A quantity of platinum equal to 1% by weight is deposited on a ZSM-12 zeolite prepared as described in the previous Example 1, using an aqueous solution of platinum tetra-amine hydroxide $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ having a platinum concentration of 0.861 g/l. A volume of 180 ml of this solution was added to 15.5 g of ZSM-12 prepared as described in step (a) of the previous Example 1, so that all the solid is covered by the solution, in order to avoid heterogeneity in the platinum distribution. The suspension thus obtained is maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent is subsequently removed by heating to about 70° C. under vacuum. The dry product is finally calcined under a stream of air with the following temperature profile 25-380° C. in two hours, 380° C. for 3 hours.

[0054] A ZSM-12 zeolite is obtained, containing 0.1% by weight of platinum.

EXAMPLE 4

Preparation of Catalyst D

MSA 100/1% Pt

a) Preparation of the MSA Acidic Component

[0055] 23.5 litres of demineralized water, 19.6 kg of aqueous solution at 14.4% by weight of TPA-OH and 600 g of aluminum tri-isopropoxide are introduced into a 100 litre reactor. The mixture is heated to 60° C. and maintained under stirring at this temperature for 1 hour, in order to obtain a limpid solution. The temperature of the solution is then brought to 90° C. and 31.1 kg of tetra-ethyl silicate are rapidly added. The reactor is closed and the stirring rate is regulated at about 1.2 m/s, the mixture being maintained under stirring for three hours at a temperature ranging from 80 to 90° C., with thermostatic control to remove the heat produced by the hydrolysis reaction. The pressure in the reactor rises to about 0.2 MPag. At the end, the reaction mixture is discharged and cooled to room temperature,

obtaining a homogeneous and relatively fluid gel (viscosity 0.011 Pa·s) having the following composition molar ratios:

$$\text{SiO}_2/\text{Al}_2\text{O}_3=101$$

$$\text{TPA.OH}/\text{SiO}_2=0.093$$

$$\text{H}_2\text{O}/\text{SiO}_2=15$$

[0056] The product is left to rest for about 6-8 hours and is then dried by maintaining it in a stream of air at 100° C. until the weight becomes constant. It is finally calcined in a muffle at 550° C. for 8 hours in air.

[0057] In this way, a porous solid is obtained, with acidic characteristics, essentially consisting of silica-alumina with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3=100$, a BET surface area of 740 m²/g, a pore volume of 0.49 ml/g, an average diameter of 2.3 nm. Upon X-ray analysis, the solid proves to be substantially amorphous, the XRD spectrum from powders does not have a crystalline structure and does not show any peak.

b) Deposition of Platinum (1% by Weight of Pt)

[0058] In order to disperse the platinum onto the acidic component, an aqueous solution of hexachloroplatinic acid (H_2PtCl_6), hydrochloric acid and acetic acid was used, in the following molar ratios: $\text{H}_2\text{PtCl}_6/\text{HCl}/\text{CH}_3\text{COOH}=1/0.84/0.05$, having a platinum concentration of 0.75 g/l. A volume of 400 ml of this solution was added to 30 g of the zeolite prepared as described in the previous step (a), so that all the solid was covered by the solution, to avoid heterogeneity in the platinum distribution. The suspension thus obtained was maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent was subsequently removed by heating to about 70° C. under vacuum. The dry product was finally calcined under a stream of air with the following temperature profile 25-350° C. in two hours, 350° C. for 2 hours, 350-400° C. in 50 min., 400° C. for 3 hours.

[0059] A silico-alumina of the MSA type is obtained, containing 1% by weight of platinum.

EXAMPLE 5

Preparation of Catalyst E

MSA 50/1% Pt

a) Preparation of the MSA Acidic Component

[0060] 23.5 litres of demineralized water, 19.6 kg of aqueous solution at 14.4% by weight of TPA-OH and 1,200 g of aluminum tri-isopropoxide are introduced into a 100 litre reactor. The mixture is heated to 60° C. and maintained under stirring at this temperature for 1 hour, in order to obtain a limpid solution. The temperature of the solution is then brought to 90° C. and 31.1 kg of tetra-ethyl silicate are rapidly added. The reactor is closed and the stirring rate is regulated at about 1.2 m/s, the mixture being maintained under stirring for three hours at a temperature ranging from 80 to 90° C., with thermostatic control to remove the heat produced by the hydrolysis reaction. The pressure in the reactor rises to about 0.2 MPag. At the end, the reaction mixture is discharged and cooled to room temperature, obtaining a homogeneous and relatively fluid gel (viscosity 0.011 Pa·s) having the following composition molar ratios:

$$\text{SiO}_2/\text{Al}_2\text{O}_3=50.5$$

$$\text{TPA.OH}/\text{SiO}_2=0.093$$

$$\text{H}_2\text{O}/\text{SiO}_2=15$$

[0061] The product is left to rest for about 6-8 hours and is then dried by maintaining it in a stream of air at 100° C. until the weight becomes constant. It is finally calcined in a muffle at 550° C. for 8 hours in air.

[0062] In this way, a porous solid is obtained, with acidic characteristics, essentially consisting of silica-alumina with a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3=50.2$, a BET of 794 m^2/g , a pore volume of 0.42 ml/g , an average diameter of 2.1 nm. Upon X-ray analysis, the solid proves to be substantially amorphous, the XRD spectrum from powders does not have a crystalline structure and does not show any peak.

b) Deposition of Platinum (1.0% by Weight of Pt)

[0063] The same procedure is adopted as described in Example 4, using 400 ml of the same aqueous solution of hexachloroplatinic acid, which are added to 30 g of the solid pre-prepared under point (a).

[0064] A silico-alumina of the MSA type is obtained, containing 1% of platinum.

EXAMPLE 6

Catalyst F

MSA 50/1% of Pt

[0065] A quantity of Pt equal to 1% by weight is deposited on an MSA acid component prepared according to step (a) of Example 5, using the same deposition procedure as that described in Example 3: 180 ml of an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ are used, whose platinum titer is 0.861 g/l , and added to 15.5 g of MSA acid solid prepared as described in step (a) of Example 5.

[0066] A silico-alumina of the MSA type is obtained, containing 1% of platinum.

EXAMPLE 7

Catalyst G

MSA 50/1% of Pt

[0067] A quantity of Pt equal to 1.5% by weight is deposited on an MSA acid component prepared according to step (a) of Example 5, using the same deposition procedure as that described in Example 4: 400 ml of an aqueous solution of hexachloroplatinic acid, with a platinum concentration of 1.125 g/l , are added to 30 g of MSA acid component.

[0068] A silico-alumina of the MSA type is obtained, containing 1.5% of Pt.

EXAMPLE 8

Catalyst H

MSA 50/1% of Ir

[0069] A quantity of Ir equal to 1% by weight is deposited on an MSA acid component prepared according to step (a) of Example 5, using an aqueous solution of hexachloroiridic acid (H_2IrCl_6), hydrochloric acid and acetic acid in the following molar ratios: $\text{H}_2\text{IrCl}_6/\text{HCl}/\text{CH}_3\text{COOH}=1/0.84/0.05$, having a concentration of iridium of 0.75 g/l . A volume of 400 ml of this solution is added to 30 g of the solid

prepared as described in the previous step (a), so that all the solid is covered by the solution, in order to avoid heterogeneity in the platinum distribution. The suspension thus obtained is maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent is subsequently removed by heating to about 70° C. in a stream of air. The dry product is finally calcined under a stream of air with the following temperature profile 25-350° C. in two hours, 350° C. for 2 hours, 350-400° C. in 50 min., 400° C. for 3 hours.

[0070] A silico-alumina of the MSA type is obtained, containing 1% by weight of Ir.

EXAMPLE 9

Catalytic Test

[0071] The catalytic tests were carried out on a continuous laboratory plant shown in FIG. 1. The system consisted of a tubular fixed bed reactor (4) with a useful volume of the charge of 20 cm^3 corresponding to a height of the catalytic bed in the isotherm section of 10 cm. The feeding of the charge, contained in the tank (1) and hydrogen to the reactor are effected by means of a dosage pump (2) and a mass flow meter, respectively. The system is also equipped with two gas lines (air and nitrogen) which are used in the regeneration phase of the catalyst. The reactor operates in an equi-current down flow system. The temperature of the reactor is regulated by means of an oven with two heating elements (3) whereas the temperature control of the catalytic bed is effected by means of a thermocouple (10) positioned inside the reactor. The pressure of the reactor is regulated by means of a valve (8) situated downstream of the reactor. The reaction products are collected in a separator (5) which operates at room temperature and atmospheric pressure. The products leaving the separator (5) pass into a condenser (6) cooled to 5° C. and are subsequently sent to a gas meter (C.L.) (7) and then to the blow-down (B.D.) (9) is the breakage disk. The distribution of the products and conversion level are determined by means of mass balance and gas chromatographic analysis of the reaction products.

[0072] Catalysts A, B and C were tested in the process of the present invention, in the equipment described above, using methyl-cyclohexane as substrate.

[0073] Before being tested, the catalysts were activated as follows:

[0074] 1) 1 hour at room temperature in a nitrogen stream;

[0075] 2) 1 hour at 50° C. in a hydrogen stream;

[0076] 3) heating from room temperature to 380° C. with a profile of 3° C./min in a hydrogen stream;

[0077] 4) the temperature is kept constant at 380° C. for 3 hours in a hydrogen stream, and is then cooled to 200° C.

[0078] During the activation, the pressure in the reactor is maintained at between 2.0 and 6.0 MPa (20 and 60 atm).

[0079] The results are indicated in Table 1 and were obtained under the following conditions:

WHSV=1 hour⁻¹

H₂/HC=1143 Nlt/kg

[0080] Pressure=60 atm

TABLE 1

| | Cat. A Temp: 300° C. | Cat. B Temp: 320° C. | Cat. C Temp: 310° C. |
|----------------------------|-------------------------|-------------------------|-------------------------|
| Conv. % | 74.4 | 79.9 | 80.4 |
| Sel. RO n-paraffins % | 3.6 | 7.9 | 8.1 |
| Sel. RO iso-paraffins % | 32.3 | 37.2 | 37.9 |
| Sel. Npth C ₇ % | 46.3 | 39.5 | 37.6 |
| Sel. Crack % | 17.2 | 14.5 | 16.2 |

[0081] With reference to Table 1, the meaning of the abbreviations is provided hereunder:

Conv. %: [(g/h Methyl-cyclo hexane fed–g/h Methyl-cyclohexane in the products)/(g/h Methyl-cyclohexane fed)]×100
RO: ring opening

Sel. RO n-paraffins %: [(g/h of C₆ and C₇ n-paraffins in the products)/(g/h of methyl-cyclohexane converted)]×100

Sel. RO iso-paraffins %: [(g/h of C₆ and C₇ iso-paraffins in the products)/(g/h of methyl-cyclohexane converted)]×100

Sel. Crack %: [(g/h of C₁, C₂, C₃, C₄ and C₅ iso-alkanes and n-alkanes)]×100

Sel. Npth C₇ %: [(g/h of ethyl-cyclopentane and isomers of dimethyl cyclopentane)/(g/h of methyl-cyclohexane converted)]×100.

[0082] The ethyl-cyclopentane and isomers of dimethyl cyclopentane are first formation products which in turn give rise to the formation of n-paraffins and iso-paraffins by the ring opening.

[0083] Unless otherwise specified, the complement to 100 of the selectivities consists of minority reaction products such as methyl-cyclopentane, cyclopentane and cyclohexane.

[0084] In the examples indicated in Table 1 and in those indicated below, the (iso-C₆+n-C₆)/(iso-C₇+n-C₇) ratio is lower than 0.1.

EXAMPLE 10

Catalytic Test

[0085] Following the procedure described in Example 9, catalysts D (MSA 100/1% Pt), E (MSA 50/1.0% Pt), F (MSA 50/1.0% Pt) and G (MSA 50/1.5% Pt) were evaluated. The results are provided in Table 2 and were obtained under the following conditions:

WHSV=1 hour⁻¹

H₂/HC=1143 Nlt/kg

[0086] P=60 atm

TABLE 2

| | Cat. D 360° C. | Cat. E 340° C. | Cat. F 320° C. | Cat. G 340° C. |
|-----------------------|-------------------|-------------------|-------------------|-------------------|
| Conv. % | 94.8 | 91.4 | 81.8 | 91.0 |
| Sel. RO n-paraffins % | 14.2 | 13.5 | 10.6 | 10.8 |

TABLE 2-continued

| | Cat. D 360° C. | Cat. E 340° C. | Cat. F 320° C. | Cat. G 340° C. |
|----------------------------|-------------------|-------------------|-------------------|-------------------|
| Sel. RO iso-paraffins % | 58.3 | 60.3 | 48.8 | 61.3 |
| Sel. Npth C ₇ % | 10.2 | 14.9 | 33.9 | 14.4 |
| Sel. Crack % | 15.5 | 11.2 | 6.7 | 10.3 |

EXAMPLE 11

Catalytic Test with MSA 100/1% Pt

Pressure Effect

[0087] Following the procedure described in Example 9, the performances of catalysts D (MSA 100/1% Pt) and F (MSA 50/1.0% Pt) were determined with variations in the pressure.

[0088] In all cases the WHSV was 1 hour⁻¹ and the H₂/HC molar ratio was 1143 Nlt/Kg. The results indicated in Table 3 show that the increase in pressure causes an increase in the conversion together with a considerable increase in the selectivity to C₆-C₇ iso-paraffins and n-paraffins.

TABLE 3

| | Cat. D Temp: 360° C. | | Cat. F Temp: 320° C. | |
|-----------------------------|-------------------------|------|-------------------------|------|
| Pressure (atm) | 20 | 70 | 40 | 60 |
| Conv. % | 74.6 | 98.1 | 76.8 | 81.8 |
| Sel. RO n-paraffins % | 4.2 | 15.7 | 8.6 | 10.6 |
| Sel. RO iso-paraffins % | 22.2 | 57.4 | 29.5 | 48.8 |
| Sel. Npth. C ₇ % | 59.0 | 3.6 | 55.3 | 33.9 |
| Sel. Crack % | 7.3 | 18.6 | 6.6 | 6.7 |

EXAMPLE 12

Catalytic Test with Catalyst C

ZSM-12/1% Pt

[0089] Following the procedure described in Example 9, catalyst C was used, varying the pressure from 20 to 70 atm. The results are indicated in Table 4.

[0090] The tests were effected under the following operating conditions: Temperature: 310° C.; WHSV=1.0 hour⁻¹; H₂/HC=1143 Nlt/Kg.

[0091] In this case, unlike the behaviour shown by the catalytic system containing MSA as acidic component, the increase in pressure had no effect on the conversion, it increases the selectivity to C₆ and C₇ iso-paraffins and n-paraffins and at the same time considerably decreases the selectivity to cracking products.

TABLE 4

| | 20 | 40 | 60 | 70 |
|-------------------------|------|------|------|------|
| Pressure (atm) | 20 | 40 | 60 | 70 |
| Conv. % | 78.9 | 80.1 | 80.4 | 80.9 |
| Sel. RO n-paraffins % | 6.6 | 7.6 | 8.2 | 10.7 |
| Sel. RO iso-paraffins % | 29.7 | 35.2 | 37.8 | 39.1 |

TABLE 4-continued

| | | | | |
|-----------------------------|------|------|------|------|
| Sel. Npth. C ₇ % | 38.9 | 38.5 | 37.6 | 35.3 |
| Sel. Crack % | 23.8 | 18.4 | 16.2 | 14.3 |

EXAMPLE 13

Catalytic Test

[0092] Following the procedure described in Example 9, catalyst H (MSA 50/1.0 Ir) was evaluated.

[0093] The results are indicated in Table 5 and were obtained under the following conditions:

WHSV=1 hour⁻¹

H₂/HC=1143 Nlt/kg

[0094] P=20 atm

TABLE 5

| | Cat. H 260° C. |
|-----------------------------|-------------------|
| Conv. % | 81 |
| Sel. RO n-paraffins % | 3.4 |
| Sel. RO iso-paraffins % | 84.2 |
| Sel. Npth. C ₇ % | 4.3 |
| Sel. Crack % | 8.0 |

EXAMPLE 14

Comparative

Preparation of Catalyst I

Mordenite/1.0% Pt

[0095] Engelhard HSZ-690HOA mordenite is used, characterized by an SiO₂/Al₂O₃ ratio=200.

[0096] In order to disperse the platinum onto this zeolite, an aqueous solution of hexachloroplatinic acid (H₂PtCl₆), hydrochloric acid and acetic acid was used, in the following molar ratios: H₂PtCl₆/HCl/CH₃COOH=1/0.84/0.05, having a platinum concentration of 0.75 g/l. A volume of 200 ml of this solution was added to 30 g of the zeolite so that all the solid was covered by the solution, to avoid heterogeneity in the platinum distribution. The suspension thus obtained was maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent was subsequently removed by heating to about 70° C. under vacuum. The dry product was finally calcined under a stream of air with the following temperature profile 25-350° C. in 2 hours, 360° C. for 3 hours.

[0097] A mordenite is obtained, containing 1.0% by weight of platinum.

EXAMPLE 15

Comparative

Preparation of Catalyst L

ZSM-23/1.0% Pt

a) Preparation of ZSM-23

[0098] The ZSM-23 zeolite is prepared according to Ernst, Verified Syntheses of Zeolitic Materials H. Robson Ed., Elsevier, (2001) page 217:

[0099] 6.4 g of Cab-o-Sil were dispersed in 78.2 g of an 0.55 M aqueous solution of NaOH. A solution containing 9.5 g of H₂O, 3.4 g of pyrrolidine and 0.7 g of Al₂(SO₄)₃*16H₂O was added to the slurry obtained. Finally, 1.7 g of H₂SO₄ were added dropwise under vigorous stirring. The slurry obtained, having a pH value of 11.6, was left to crystallize under hydro-thermal conditions at 180° C. for 2 days in an AISI 316 steel autoclave, subjected to a rotating movement.

[0100] The ZSM-23 zeolite at this stage of the synthesis is in soda form, in order to obtain the acidic form, it is subjected to the treatment described hereunder.

[0101] 100 g of ZSM-23 are redispersed in 1000 g of an 0.2 M solution of ammonium acetate. The mixture is left under stirring at 40° C. for about 3 hours. The solid phase is then separated and the operation is repeated twice. The solid is finally redispersed in demineralized water for a last washing.

[0102] The damp panel obtained consists of ZSM-23 in ammonia form. In order to obtain the zeolite in acidic form, the solid is dried at 150° C., and is then calcined at 550° C. for 5 hours in air, thus eliminating the ammonia and possible present of organic templating agent still blocked.

b) Deposition of the Platinum (1.0% Pt)

[0103] A quantity of platinum equal to 1% by weight is deposited on a ZSM-23 zeolite prepared as described in the previous step (a), using an aqueous solution of platinum tetra-amine hydroxide Pt(NH₃)₄(OH)₂, having a platinum concentration of 0.861 g/l. A volume of 180 ml of this solution was added to 15.5 g of ZSM-23 prepared as described in the previous step (1), so that all the solid is covered by the solution, to avoid heterogeneity in the platinum distribution. The suspension thus obtained was maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent was subsequently removed by heating to about 70° C. under vacuum. The dry product was finally calcined under a stream of air with the following temperature profile 25-380° C. in 2 hours, 380° C. for 3 hours.

[0104] A ZSM-23 zeolite is obtained, containing 1% of platinum.

EXAMPLE 16

Comparative

Preparation of Catalyst M

[0105] For the preparation of this catalyst, a commercial amorphous silico alumina (PK-200 of Kalichemie) is used, having the following characteristics:

[0116] 4) the temperature is kept constant at 380° C. for 3 hours in a hydrogen stream, and is then cooled to 200° C.

[0117] During the activation, the pressure in the reactor is maintained at between 2.0 and 6.0 MPa (20 and 60 atm).

[0118] The results are indicated in Table 6 and were obtained under the following conditions:

WHSV=1 hour⁻¹

[0119] H₂/HC=1143 Nlt/kg

TABLE 6

| | Cat. M PK-200/Pt 360° C. 20 atm | Cat. I MOR/Pt 290° C. 20 atm | Cat. L ZSM-23/Pt 320° C. 60 atm | Cat. D MSA-100/Pt 360° C. 20 atm | Cat. B ZSM-12/Pt 320° C. 60 atm |
|----------------------------|--|---------------------------------------|--|---|--|
| Conv. % | 70.2 | 70.4 | 67.4 | 74.6 | 79.9 |
| Sel. RO n-paraffins % | 2.2 | 3.4 | 5.2 | 4.2 | 7.9 |
| Sel. RO iso-paraffins % | 8.0 | 18.2 | 24.4 | 22.2 | 37.2 |
| Sel. Npth C ₇ % | 77.5 | 55.3 | 48.1 | 59.0 | 39.5 |
| Sel. Crack % | 3.8 | 16.4 | 31.3 | 7.3 | 14.5 |

[0106] weight % composition: 90% SiO₂, 10% Al₂O₃

[0107] molar ratio SiO₂/Al₂O₃: 15.3

[0108] surface area: 450 m²/g

[0109] In order to disperse the platinum onto this silico-alumina, an aqueous solution of hexachloroplatinic acid (H₂PtCl₆), hydrochloric acid and acetic acid was used, in the following molar ratios: H₂PtCl₆/HCl/CH₃COOH=1/0.84/0.05, having a platinum concentration of 0.75 g/l. A volume of 200 ml of this solution was added to 30 g of the silico-alumina so that all the solid was covered by the solution, to avoid heterogeneity in the platinum distribution. The suspension thus obtained was maintained under stirring for about an hour at room temperature and subsequently degassed by suction under vacuum (about 18 mmHg) at room temperature. The solvent was subsequently removed by heating to about 70° C. under vacuum. The dry product was finally calcined under a stream of air with the following temperature profile 25-350° C. in 2 hours, 360° C. for 3 hours.

[0110] A silico-alumina is obtained, containing 1.0% by weight of platinum.

[0120] An examination of the data of Table 6 demonstrates that the catalytic systems based on Pk-200, mordenite (MOR) and ZSM-23 show much lower performances in terms of selectivity towards the ring opening or, as in the case of ZSM-23 a much higher selectivity to cracking products with respect to the performances of the catalytic systems object of the present invention, in particular B and D.

EXAMPLE 18

Comparative

[0121] In this example, the results obtained in U.S. Pat. No. 5,763,731, Example 11 are indicated as a comparison, wherein an Ir/amorphous SiO₂—Al₂O₃ catalyst, containing 0.9% by weight of Ir and having an SiO₂/Al₂O₃ ratio of 85/15, is tested in the ring opening of n-butyl-cyclohexane (BCH). The test preparation and conditions are described in Example 1 of said patent.

[0122] At 275° C. and a total LHSV of 4.2, a conversion of BCH of 42.2% is obtained, together with a selectivity of products deriving from the ring opening of 0.45.

[0123] A comparison between these results and those obtained in Example 13 of the present patent application shows that the catalyst containing iridium, representative of the invention, provides much higher conversion and selectivity results than those of the comparative catalyst. The diversity of the results is such that only a minimum part can be attributed to the diversity of the substrates.

EXAMPLE 19

[0124] In this example, the results obtained in U.S. Pat. No. 5,763,731, Example 7 are indicated as a comparison, wherein a Pt/ECR-32 catalyst, containing 0.9% by weight of Ir is tested in the ring opening of n-butyl-cyclohexane (BCH). The test preparation and conditions are described in Example 6 of said patent. The ECR-32 zeolite is described in U.S. Pat. No. 4,931,267

EXAMPLE 17

Comparative

Catalytic Test

[0111] The catalytic tests were carried out as described in Example 9, on the continuous laboratory plant shown in FIG. 1.

[0112] Catalysts I, L and M are tested in the process of the present invention using methyl cyclohexane as substrate. Before being tested the catalysts were activated as follows:

[0113] 1) 1 hour at room temperature in a nitrogen stream;

[0114] 2) 1 hour at 50° C. in a hydrogen stream;

[0115] 3) heating from room temperature to 380° C. with a profile of 3° C./min in a hydrogen stream;

[0125] At 275° C. and a total LHSV of 2.9, a conversion of BCH of 90.0% is obtained, together with a selectivity of products deriving from the ring opening of 0.01.

[0126] On comparing these results with those obtained in Example 12, it can be observed that the catalyst containing 1% of Pt and ZSM-12 zeolite of the present invention provides much higher selectivity results, not proportional to the diversity of the substrates.

1) A process for the upgrading of distillates having a boiling point which varies from 100 to 450° C., by the opening of naphthene rings of compounds containing them to give paraffinic mixtures, said process consisting in treating the distillates, in the presence of hydrogen, with a catalytic system comprising:

- a) one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re
 - b) a silico-aluminate of an acidic nature selected from a zeolite belonging to the MTW group and a completely amorphous, micro-mesoporous silico-alumina, having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 30 to 500, a surface area greater than 500 m²/g, a pore volume within the range of 0.3-1.3 ml/g, an average pore diameter of less than 40 Å.
- 2) The process according to claim 1, wherein the acidic component (b) is a ZSM-12 zeolite.
- 3) The process according to claim 1, wherein the acidic component (b) is a silico-alumina with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranging from 50/1 to 300/1.
- 4) The process according to claim 1, wherein the acidic component (b) is a silico-alumina with a porosity ranging from 0.4 to 0.5 ml/g.
- 5) The process according to claim 1, wherein the acidic component (b) is a silico-alumina whose XRD spectrum from powders does not have a crystalline structure and does not show any peak.
- 6) The process according to claim 1, wherein the metal is platinum, iridium or mixtures thereof.
- 7) The process according to claim 1, wherein the metal or mixture of metals is in a quantity ranging from 0.1 to 5% by weight with respect to the total weight of the catalytic composition.
- 8) The process according to claim 7, wherein the metal or mixture of metals is in a quantity ranging from 0.3 to 1.5% by weight with respect to the total weight of the catalytic composition.
- 9) The process according to claim 1, wherein the distillates are hydrocarbon cuts selected from naphthas, diesel, kerosene, jet fuel, light cycle oil, HVGO, FCC heavy fraction.

10) The process according to claim 1, carried out at a temperature ranging from 240 to 380° C., at a pressure ranging from 20 to 70 atm, a WHSV ranging from 0.5 to 2 hours⁻¹ and a hydrogen/charge ratio (H_2/HC) ranging from 400 to 2000 Nlt/kg.

11) The process according to claim 10, wherein the acidic component (b) is a zeolite of the MTW type, the pressure is greater than 40 atm and less than or equal to 70 atm, and the temperature ranges from 240 to 320° C.

12) The process according to claim 10, wherein the acidic component (b) is a silico-alumina, the pressure is greater than 40 atm and less than or equal to 70 atm, and the temperature ranges from 300 to 380° C.

13) A catalytic composition comprising:

a) one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re

b) a zeolite belonging to the MTW group.

14) A catalytic composition comprising:

a) one or more metals selected from Pt, Pd, Ir, Ru, Rh and Re

b) a completely amorphous, micro-mesoporous silico-alumina, having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 30 to 500, a surface area greater than 500 m²/g, a pore volume greater than 0.6 and less than or equal to 1.3 ml/g, an average pore diameter of less than 40 Å, an XRD spectrum from powders which does not have a crystalline structure and does not show any peak.

15) A catalytic composition comprising:

a) one or more metals selected from Ir, Ru, and Rh

b) a completely amorphous, micro-mesoporous silico-alumina, having a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranging from 30 to 500, a surface area greater than 500 m²/g, a pore volume within the range of 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, an XRD spectrum from powders which does not have a crystalline structure and does not show any peak.

16) A process for preparing the catalytic compositions of claim 13, 14, 15, which comprises subjecting the acidic component (b) to impregnation or ion exchange with a solution of a compound of one or more metals selected from Pt, Pd, Ir, Rh and Re.

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