

PARA-XYLENE SELECTIVE REFORMING/AROMATIZATION

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Technical Field

The present invention relates to a unique reforming or aromatization process for producing C₈ aromatics which are enriched to above equilibrium levels in para-xylene from feeds containing C₈ non-aromatics, the catalyst used in such a process and the methods of forming the catalyst.

Background Of The Invention

Para-xylene is useful for the production of terephthalic acid. Terephthalic acid is used for the production of polyester resins and fibers such as Dacron. Para-xylene is a byproduct of reforming processes for the manufacture of fuels, particularly for the manufacture of gasoline. Para-xylene occurs in approximately equilibrium amounts, about 22%, in the C₈ aromatics fraction of a typical reformat stream. (All %s mentioned herein are weight %s.)

Para-xylene and other aromatics can be recovered from reformates using a combination of extraction and distillation steps. Para-xylene can be separated from other C₈ aromatics and purified by processes which include crystallization or adsorption processes. The other C₈ aromatics, which now contain para-xylene in less than equilibrium amounts, are typically recycled through an isomerization unit in order to bring the para-xylene percentage back up to near equilibrium levels. The resulting stream is then

recycled to the separation and purification unit to recover additional para-xylene.

5 The efficiency of para-xylene recovery and purification would be increased and the cost would be decreased if the C_8 aromatics feedstream was enriched in para-xylene. In the best case, with a very rich para-xylene stream, the recycle through the isomerization step could be eliminated entirely. Since conventional
10 reforming and aromatization produces para-xylene at only approximately equilibrium levels a conventional reforming or aromatization process does not give the desired improved efficiency of para-xylene recovery. A reforming/aromatization catalyst and process which would
15 give C_8 aromatics which are enriched in para-xylene above equilibrium levels would thus be highly desirable.

It is known to produce xylenes with para-xylene levels above equilibrium by disproportionation of toluene. This process produces xylenes and benzene by
20 a transalkylation mechanism. Patents which illustrate the production of para-xylene rich xylene streams from the disproportionation of toluene include U.S. Patents 4,011,276; 4,016,219; 4,052,476; 4,029,716; 4,067,919; 4,097,543; 4,098,837; 4,127,616; 4,160,788; 4,182,923;
25 4,361,713; 4,365,104; 4,367,359; 4,370,508; 4,308,685 and 4,384,155, all of which are incorporated by reference.

U.S. Patent 4,007,231 discloses the use of an antimony oxide modified zeolite, for example,
30 HZSM-5, to produce para-xylene rich C_8 aromatics from toluene and from C_3 - C_{10} paraffins, olefins, or naphthenes. Also, U.S. Patent 4,117,026 utilizes an intermediate pore zeolite, for example, HZSM-5, which has been modified by metal oxides, precoking or using a
35 large crystal form to produce para-xylene rich C_8

aromatics from toluene or high molecular weight olefinic or paraffinic feeds. In this patent a dodecane feed shows 63% para-xylene enrichment of the C₈ aromatics.

5 The catalyst does not contain a platinum group component and is not utilized for processing a C₅-C₉ predominantly paraffinic/olefinic hydrocarbon feedstock.

Some catalysts are known to be shape selective for the isomerization of ethylbenzene into para-xylene rich xylenes. Isomerization catalysts and process of this nature are set forth in U.S. Patent 4,101,595; 10 5,028,573; 5,082,984; 4,783,571 and 5,043,512.

None of the prior art is concerned with an aromatization process or a reforming process which will 15 produce acceptably high yields of para-xylene rich xylenes starting with a C₈ non-aromatics containing feed such as a typical reformer feedstock.

Disclosure Of Invention

20 The present invention is directed to overcoming one or more of the problems as set forth above.

In accordance with an embodiment of the present invention a method is set forth of reforming or 25 aromatizing a C₅-C₉ predominantly paraffinic or olefinic hydrocarbon feedstock containing C₈ non-aromatics to produce a product stream which is enriched in para-xylene. The feedstock is contacted under reforming or aromatization conditions with a catalyst which comprises 30 an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron. The catalyst is capable of converting a paraffinic feed in 35 a reforming or aromatization operation under reforming or aromatization conditions to a product which includes

xylenes which are enriched in para-xylene. The catalyst has an activity sufficient to produce a yield of benzene-toluene-xylenes-ethyl benzene (BTX) of at least about 30% from the feedstock, based on the C_6-C_8 non-aromatics content of the feedstock, on a hydrogen free basis. At least about 15% of the BTX consists of xylenes with the xylenes being at least about 30% para-xylene.

In accordance with another embodiment of the present invention a catalyst is set forth which is useful for reforming and aromatization and which comprises an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron. The catalyst is capable of converting a predominantly paraffinic or olefinic feed in a reforming or aromatization operation under reforming or aromatization conditions to a product which includes xylenes which are enriched in para-xylene. The catalyst has an activity sufficient to produce a yield of benzene-toluene-xylenes-ethyl benzene (BTX) from a hydrocarbon feedstock containing C_6-C_8 non-aromatics of at least about 30%, based on the C_6-C_8 non-aromatics content of the feedstock on a hydrogen free basis. At least about 15% of the BTX consists of xylenes with the xylenes being at least about 30% para-xylene.

In accordance with still another embodiment of the present invention a method is set forth of producing a catalyst having an activity under reforming or aromatization conditions as set forth above. The method comprises contacting a catalyst comprising an intermediate pore size molecular sieve

support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron with a hydrocarbon feedstock until the catalyst becomes coated with coke sufficiently so that it is capable of converting toluene by disproportionation to xylenes which are rich in para-xylene. The catalyst, prior to the contacting, is capable of converting an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5 to 10, a pressure of 0 to 800 psig and a hydrogen to hydrocarbon molar ratio within the range from 1:1 to 20:1. The coked catalyst is exposed to a hydrogen atmosphere for a time sufficient so that, following such exposure, it is capable of converting at least 30% of an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.

A large number of molecular sieves are known to have use as catalysts in various hydrocarbon conversion reactions such as disproportionation, aromatization including reforming, catalytic cracking, hydrocracking, dehydrocyclization, isomerization and dewaxing. Typical intermediate pore size molecular sieves of this nature include ZSM-5, silicalite, generally considered to be a high silica to alumina ratio form of ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, SSZ-32, SAPO-11, SAPO-31, SAPO-41, and the like. Zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38 are described in U.S. Patents Nos. 3,700,585; 3,894,938; 3,849,290; 3,950,241; 4,032,431; 4,141,859; 4,176,050; 4,181,598; 4,222,855; 4,229,282; and 4,247,388 and in British Patent 1,469,345. The use of such catalysts, particularly para-selective

forms of such catalysts which contain a platinum group aromatization promoting component, for the production of para-xylene enriched xylene products from a hydrocarbon, generally paraffinic feedstock, is not known and has
5 generally not been contemplated.

Operating in accordance with the present invention one can begin with a typical primarily non-aromatic reformer feed, for example a C_3 - C_9 feed with
10 about a 300°F end point, and reform the feed to form a product which contains para-xylene in above equilibrium amounts. The C_3 - C_9 feed can also contain minor amounts of $C_{10}+$ components. Generally at least about 30% of the C_8 aromatics will be in the form of para-xylene. The BTX
15 fraction of the feed can be separated, for example by distillation, and utilized to produce benzene, toluene and xylenes; particularly para-xylene, which can then be utilized in chemical synthesis. The remainder of the reformat will generally be useful as a gasoline
20 blending stock. This result is particularly surprising since, as will be demonstrated below, if one starts with a pure n-heptane (C_7) feed under the same conditions, the resulting product, while it contains substantial amounts
25 of toluene and a C_8 aromatics fraction which is enriched in para-xylene, contains so little xylenes whereby the process would be highly inefficient in the manufacture of para-xylene. This indicates that what is occurring is not reforming to form toluene followed by
30 disproportionation of the toluene to form benzene and a para-xylene rich xylene fraction, but rather direct conversion of the paraffins in the feed, and apparently of lower molecular weight paraffins as well, to xylenes which are enriched in para-xylene. It is also
35 surprising and unexpected that a catalyst which has been selectivated for producing para-xylene

enriched xylenes by disproportionation of toluene and in which is included a platinum group component would have sufficient reforming/aromatization activity to produce acceptable yields of aromatics.

Brief Description of Drawings

The invention will be better understood by reference to the figures of the Drawings, wherein:

Figure 1 illustrates experimental results as described in Example 7: and

Figure 2 illustrates experimental results as described in Example 8.

Detailed Description Of The Invention

A novel catalyst useful for reforming and/or aromatization forms one aspect of the present invention. The catalyst comprises an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin, boron, and mixtures thereof.

Zeolites can be characterized by their absorption characteristics at relatively low temperatures, for example from 77°K to 420°K, as described in , for example, Zeolite Molecular Sieves, Donald W. Breck, First Edition, John Wiley & Sons, 1974. These absorption characteristics are a function of the kinetic diameters of the particular molecule being absorbed and of the channel dimensions of the molecular sieve. Intermediate pore size molecular sieves useful in the practice of the invention in the H-form will typically admit molecules having kinetic diameters of 5.0 to 6.0Å with little hindrance. Examples of such compounds (and their kinetic diameters in Å) are: n-hexane (4.3), 3-methylpentan

(5.5), benzene (5.8), and toluene (5.8). Compounds having kinetic diameters of about 6.0 to 6.8Å can be admitted into the pores, depending on the particular sieve, but do not penetrate as quickly and in some cases are effectively excluded. Compounds having kinetic diameters in the range of 6.0 to 6.8Å include: cyclohexane (6.0), 2,3-dimethylbutane (6.1), 2,2-dimethylbutane (6.2), m-xylene (6.1), 1,2,3,4-tetramethylbenzene (6.4) and o-xylene (6.8). Generally, compounds having kinetic diameters of greater than about 6.8Å do not penetrate the pore apertures and thus are not absorbed into the interior of the molecular sieve lattice. Examples of such larger compounds include: hexamethylbenzene (7.1), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1).

Specific molecular sieves which are useful in the process of the present invention include the zeolites ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-25, SSZ-32, and other molecular sieve materials based upon aluminum and/or magnesium phosphates such as SAPO-11, SAPO-31, SAPO-41, MAPO-11 and MAPO-31. Such molecular sieves are described in the following publications, each of which is incorporated herein by reference: U.S. Patents Nos. 3,702,886; 3,709,979; 3,832,449; 3,950,496; 3,972,983; 4,076,842; 4,016,245; 4,046,859; 4,234,231; 4,440,871 and U.S. Patent Applications Serial Nos. 172,730 filed March 23, 1988 and 433,382, filed October 24, 1989. In most cases, these molecular sieves must be further treated to impart para-selectivity as discussed below.

The sieves are preferably bound with any of a variety of well-known inorganic oxide binders. Appropriate binders include inorganic compositions with which the molecular sieve can be combined,

dispersed or otherwise intimately admixed. Preferred
oxide binders include alumina, silica, naturally
occurring and conventionally processed clays, for
5 example, bentonite, kaolin, sepiolite, attapulgite and
halloysite.

The catalysts according to the present
invention contain one or more platinum group metals,
preferably iridium, palladium, and most preferably
10 platinum. They are quite selective with regard to
aromatization via dehydrocyclization and are also very
stable under the dehydrocyclization reaction conditions.
The preferred percentage of the platinum group metals,
such as platinum, in the catalyst is between 0.1 wt.%
15 and 5 wt.%, more preferably from 0.3 wt.% to 2.5 wt.%.

Platinum group metals are preferably
introduced into the crystalline silicate by
impregnation, occlusion, or exchange in an aqueous
solution of an appropriate salt. When it is desired to
20 introduce two platinum group metals, or a platinum group
metal along with another metal such as gallium, zinc or
indium, into the crystalline silicate, the operation may
be carried out simultaneously or sequentially.
Preferably, the platinum group metal is finely dispersed
25 within, and on, the crystalline silicate.

By way of example, platinum can be introduced
by impregnation with an aqueous solution of
tetraammineplatinum (II) nitrate, tetraammineplatinum
(II) hydroxide, dinitrodiamino-platinum or
30 tetraammineplatinum (II) chloride. In an ion exchange
process, platinum can be introduced by using cationic
platinum complexes such as tetraammineplatinum (II)
nitrate. When platinum is introduced into the silicate
by occlusion a platinum complex is preferably

introduced into the crystalline silicate during its formation.

5 The other component of the catalyst is a
component selected from the group consisting of gallium,
zinc, indium, iron, tin and boron. This component serves
the purpose of increasing the yield of aromatics in the
aromatization or reforming process. As described by P.
Meriaudeau, G. Sapaly, and C. Naccache in the Journal
10 of Molecular Catalysts, 81 (1993) 293-300, Ga may play
several roles. Replacing Al by Ga in the framework of
ZSM-5 can modify catalytic activity by reducing the
catalyst acidity (C.T.W. Chu and C.D. Chang, J. Phys.
Chem. 89 (1995) 1569) and non-framework Ga may impart
15 dehydrogenation activity to the catalyst (D.K. Simmons,
R. Szostak, P.K. Agrawal, and T.L. Thomas, J. Catalysis
106 (1987) 287). As described by E. Iglesia, J.E.
Baumgartner, and G.L. Price in the J. Catalysis 134
(1992) 549-571, Ga may promote dehydrogenation by
20 facilitating H atom recombination to give H₂. The
gallium, indium, zinc, iron, tin and boron may be
functioning by any or all of the above mentioned roles
or by other yet to be discovered roles which serve to
increase aromatics yields.

25 The Ga may be introduced into the catalyst by
any suitable method such as impregnation, ion exchange,
or by using a Ga source in place of Al in the
preparation of the zeolite structure. The preferred
method is by substitution of Ga for Al in the
30 preparation of the zeolite. For example, a Ga ZSM-5
with Ga in the framework can be prepared by the
procedure of D.K. Simmons, R. Szostak, P.K. Agrawal and
T.L. Thomas as described in the Journal of catalysis,
106 (1987), 287. A framework Ga ZSM-5 may also be
35 prepared by using a Ga salt in place of the Al

in the procedure for producing ZSM-5 as described in U.S. Patent 3,703,886, issued April 14, 1967 to R.J. Argauer and G.R. Landolt. Ga may be impregnated onto the ZSM-5 zeolite by the procedure of U.S. Patent 4,174,057, issued November 20, 1979 to E.E. Davies and A.J. Kolombos which is incorporated herein by reference. Ga may also be exchanged or impregnated into the zeolite by the procedure of U.S. Patent 4,891,463, issued January 2, 1990 to C.T-W Chu which is incorporated herein by reference. In all of these methods there is potential for the Ga to occupy both framework and non-framework sites in the working catalyst. The preferred method gives a predominance of the Ga in the framework of the freshly prepared Ga ZSM-5. However, in the working form of the Ga ZSM-5, the Ga may occupy both framework and non-framework sites.

Zinc can be introduced into the catalyst in the manner set forth in U.S. Patent 4,720,602 issued January 19, 1988 to C. T-W. Chu, which patent is hereby incorporated herein by reference.

Indium can be introduced into the catalyst in the manner set forth in U.S. Patent 4,822,942, issued April 18, 1989 to Ralph M. Dessau and Ernest W. Valyocsik, which patent is hereby incorporated herein by reference. The Indium may also be introduced by standard impregnation or ion exchange methods.

Iron can be introduced into the catalyst in the manner set forth in U.S. Patent 4,665,255, issued May 12, 1987 to Clarence D. Cheng and Joseph N. Miale, which is incorporated herein by reference. The iron may also be introduced by conventional impregnation or ion exchange methods.

A borosilicate zeolite of intermediate pore structure can be synthesized by the procedure set

forth in U. S. Patent 5,187,132, issued February 16, 1993 to Stacey I. Zones, et al, which is incorporated herein by reference.

5 Tin may be introduced into the catalyst using a tin salt such as stannous chloride or acetate in conventional impregnation or ion exchange methods.

 The preferred component is gallium. The gallium, zinc, indium, iron, tin or boron is generally
10 present in an amount from about 0.1 wt.% to about 10 wt.%, preferably from about 1 wt.% to about 5 wt.%, of the total catalyst.

 The catalyst of the present invention is used in the acidic or partially neutralized acidic form. The
15 zeolite or molecular sieve component of the catalyst is typically prepared in the neutral or non-acidic form. In order to obtain the acidic form of the catalyst, the zeolite or molecular sieve component is ion exchanged to produce the ammonium salt form. As a result of
20 calcination, the acid form of the catalyst is produced.

 The catalyst in accordance with the present invention can be coked to modify its properties. Coking can be accomplished by contacting the feed with toluene or any other hydrocarbon feed under conditions which
25 include a temperature of about 500°C to about 700°C (preferably 500°C to 600°C), a pressure of 0 to 1,000 psig, (preferably 50 to 600 psig) a hydrogen to hydrocarbon mole ratio of 0 to 5 (preferably 0 to 1) and a liquid hourly space velocity of 0.1 to 20 (preferably
30 0.5 to 5). As a result of the coking the catalyst will convert a C₅-C₉ hydrocarbon feed in a reforming or aromatization operation under reforming or aromatization conditions to a product which includes xylenes which are enriched in para-xylene.

The catalyst, whether produced by coking or by other methods known in the art as set forth in the various patents showing para-selectivity incorporated
5 above, also has an activity sufficient to provide a BTX yield, based on the C₆-C₈ non-aromatics fraction of the feed, of at least about 30% (generally 40% to 75%) on a hydrogen-free basis and at least about 35% (generally 35% to 70%) on a hydrogen inclusive basis. At least
10 about 15% of the BTX is generally xylenes. The para-xylene content of the xylenes will generally be at least about 30% (generally 25% to 80%).

Typical feedstocks which may be utilized with the catalyst preferably include a C₈ paraffin component.
15 Substantially any conventional reformer feedstock can be utilized. The feedstock utilized is predominantly paraffinic or olefinic, by which is meant it generally has no more than about 30% aromatics, usually no more than about 20% aromatics. It will generally comprise C₃-
20 C₈ hydrocarbons and will have an endpoint of about 300°F. A preferred feed can comprise at least about 20% C₈ hydrocarbons and the process then being carried out is primarily a dehydrocyclization process for forming aromatics. When a full boiling range C₃-C₈ feedstock is
25 utilized the BTX fraction can be readily separated by conventional extractive distillation. A raffinate is also produced which is useful as a gasoline blending stock. The raffinate will generally have a relatively low octane, which is, however, sufficient so that it can
30 be utilized with an appropriate oxygenated compound such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) or tertiary amyl methyl ether (TAME) to provide a low aromatics content gasoline having an octane value high enough for use in motor vehicles.

A coked catalyst as set forth above can be produced by reacting a catalyst comprising an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron with a hydrocarbon until the catalyst becomes coated with coke sufficiently so that it is selectivated so as to be capable of disproportionating toluene to xylenes which are rich in para-xylene.

10 The catalyst, prior to being coked, must have an activity sufficient so that it is capable of converting at least about 30% of a n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5 to 2, a pressure of 75 psig and a

15 hydrogen to hydrocarbon mole ratio of 8:1.

In order to improve para-xylene selectivity by coking, the hydrocarbon coking agent is passed over the catalyst at a temperature in the range from about 500°C to about 600°C and a pressure in the range from about 50

20 psig to about 600 psig. Hydrogen may also be added preferably keeping the hydrogen to hydrocarbon molar ratio in the range from 0 to 1, more preferably near 0. The lower hydrogen to hydrocarbon ratios, especially near 0, favor achieving para-xylene selectivity more

25 rapidly. The progress in improving para-xylene selectivity can be measured by passing toluene or a reforming feed over the catalyst at the high temperature coking conditions and measuring the para-xylene content of the C₈ aromatics. As

30 the catalyst becomes more para-xylene selective, the para-xylene content of the C₈ aromatics will typically increase from its equilibrium value of about 22% to about 60% or higher. In one version of the process, toluene is used as the coking agent

and the para-xylene content of the xylenes produced by disproportionation of the toluene is a measure of achieving para-xylene selectivity. This can be done
5 even though the catalysts of the present invention frequently give very low xylene yields from toluene. Ideally, the coking is carried out only to the extent that the catalyst provides sufficient para-xylene selectivity without a major loss in activity as measured
10 by the conversion of n-octane or a reformer feed to xylenes. However, in practice, the coking is frequently accompanied by very significant losses in activity, perhaps down to where the catalyst will convert less than 10% of n-octane under reforming
15 conditions such as 500°C, 50-100 psig, LHSV = 2, and a hydrogen to hydrocarbon ratio of 4.

It has been found that exposing the coked catalyst to a hydrogen atmosphere, either alone or in the presence of the coking agent or other hydrocarbons
20 such as a reformer feedstock, for a sufficient time will result in the catalyst being reactivated to the degree of being capable of converting an n-octane feed to produce at least 30%, preferably 40%, BTX yield on a hydrogen free basis and at least 25%, preferably 35%,
25 BTX yield on a hydrogen inclusive basis from an n-octane feed at a temperature of 500°C, a liquid hourly space velocity of 0.5 to 10, a pressure of 0 to 800 psig and a hydrogen to hydrocarbon molar ratio of 1:1 to 20:1.

Exposing of the coked catalyst to a reducing
30 atmosphere can take place in any of the following manners under the conditions as specified in following:

- 1) The deactivated catalyst can be reactivated by exposing it to a hydrogen atmosphere at temperatures from about 500°C to about 600°C. In a

preferred case, it can be exposed to a hydrogen flow of 5-100 sccm (standard cubic centimeters per minute) per cubic centimeter of catalyst at 500-600°C and

5 50-200 psig for 10-100 hours. The conditions and the length of time needed to achieve reactivation will depend on the degree of deactivation of the catalyst. For a given state of deactivation, shorter times will be required with the higher temperatures, pressures, and

10 flow rates. It should be recognized that higher hydrogen flow rates will not be harmful as long as the back pressure does not become excessive and the catalyst bed is not physically disrupted. Pressures higher than 200 psig, for example 500-1000 psig, may also be used if

15 it is practical in the equipment being used. The degree of success in reactivation is measured by turning in a feed such as n-octane and measuring the activity and yields. If more activation is needed, the feed can be stopped and the hydrogen treatment continued until the

20 BTX yields from n-octane or a reforming feed reach about 30%, preferably 40%, or higher.

2) The reductive activation can also be accomplished by increasing the hydrogen to hydrocarbon ratio in the reforming process. A preferred version of

25 this is to increase the hydrogen rate, while holding the feed rate constant, until the catalyst begins to reactivate, and then holding under these conditions or continuing to increase the hydrogen rate until activity is recovered. To accomplish the activation, the

30 hydrogen to hydrocarbon ratio may be increased up to levels of 10-100:1. Even higher hydrogen to hydrocarbon ratios do no harm as long as the back pressure does not become excessive and the catalyst bed is not physically disturbed. This method of activation is especially

35 useful when the activation

described under 1) above is not sustained for a practical length of time. However, the reductive activation by increasing the hydrogen to hydrocarbon ratio during reforming may also be used in place of 1).

The reductive activation can also be accomplished by hydrogen treatments during the coking step for increasing para-xylene selectivity. In a preferred version of this, the coking by hydrocarbon is periodically interrupted for hydrogen treatments at the coking temperature. For example, toluene coking at about 600°C can be carried out until the para-xylene selectivity reaches 30%, preferably 40%, or higher (expressed as % of total xylenes). The toluene is turned off and the catalyst is treated with hydrogen at 600°C, typically for 10 to 100 hours. As a result, of this high temperature hydrogen treatment of the partially selectivated catalyst, the para-xylene selectivity may temporarily decrease but will be rapidly regained when the toluene feed is restarted at 600°C. The alternating of toluene coking with hydrogen treatment may be repeated more than once, but one time is typically satisfactory.

Substantially any catalyst which is para-selective for toluene disproportionation can be used in the practice of the invention. For example, any catalyst which can be coked to provide para-selectivity during a toluene disproportionation process can be used in the process of the present invention. Examples of such catalysts are found in U.S. Patents 4,117,026 and 4,097,543 of Haag and Olson, both of which are incorporated herein in their entireties by reference. The coked catalysts of the present invention are not "para-selective" as that term is known in the art (although they do exhibit

para-selectivity) but are instead better considered as being para-modified by first being coked to produce para-selectivity and then being reduced so as to be
5 useful for selective reforming/aromatization to form a para-xylene enriched reformat/aromatization product. In general, the term "para-modified" as used herein means that the catalyst, when used in accordance with the present invention, will produce a BTX fraction
10 in which at least 30% of the xylenes constitutes para-xylene. Indeed, as is shown in the examples well over 60% of the C₈ aromatics produced can be para-xylene. Attaining such a higher percentage of para-xylene is generally desirable. Other para-
15 selective catalysts can also be utilized, for example, catalysts as set forth in previously mentioned U.S. Patents 4,011,276; 4,016,219; 4,052,476; 4,029,716; 4,067,919; 4,097,543; 4,098,837; 4,127,616; 4,160,788; 4,182,923; 4,361,713; 4,365,104; 4,367,359; 4,370,508;
20 4,308,685 and 4,384,155, all of which have previously been incorporated by reference.

The use of large crystal size zeolites having a minimum crystal dimension of greater than about 0.5 micron, generally in the approximate range of 1-20
25 microns and particularly 1-6 microns is generally preferred as adding to the para-selectivity.

In assessment of zeolite crystal size, conventional scanning electron microscopy (SEM) techniques can be used, the minimum crystal dimension of
30 a given crystal being taken as the dimension of reference. The crystalline aluminosilicate zeolites used in the present invention in substantial proportion are essentially characterized by a minimum crystal dimension of greater than about 0.5 micron. It is
35 contemplated that the amount of zeolite of such crystal size will be such as to exert a directive

influence in the desired selective production of paradialkyl substituted benzenes. Generally, the amount of zeolite of such crystal size will be present in
5 predominate proportion, i.e., in an amount exceeding 50 weight percent, and preferably may constitute up to 100 weight percent of the total zeolite employed.

The coked crystalline aluminosilicate zeolites employed, particularly those having a minimum
10 crystal dimension of greater than about 0.5 micron, have undergone modification prior to use by selective precoking thereof to deposit at least about 1 weight percent and generally between about 2 and about 40 weight percent of coke thereon, based on the weight of
15 total catalyst. If the zeolite is employed in substantially pure form or in combination with a low coking binder, such as silica, then the weight percent of coke deposited is generally in the range of 2 to 20 weight percent. When the zeolite is combined with a
20 binder of high coking tendencies, such as alumina, coke deposition content of the total catalyst, prior to its being exposed to a reducing environment, is in the approximate range of 10 to 40 weight percent. Precoking can be accomplished by contacting the catalyst with a
25 hydrocarbon charge, e.g., toluene, under high severity conditions at a reduced hydrogen to hydrocarbon concentration, i.e., 0 to 1 mole ratio of hydrogen to hydrocarbon for a sufficient time to deposit the desired amount of coke thereon.

30 Following coking, if necessary to recover activity, the catalyst is exposed to a reducing atmosphere as described elsewhere herein thereby reducing the coke content to provide the para-modified catalyst. The exposure to the reducing atmosphere is
35 continued until the coked catalyst activity for

converting n-octane to other products has risen to at least 30 wt.% but is not continued to an extent which would significantly reduce the para-selectivity of the catalyst.

The ZSM-5 silicalite structure is the preferred zeolite for the reforming/aromatization/dehydrocyclization reaction. The ZSM-5 preferably has a silica to alumina mole ratio of between 10 and 20,000, generally between 10 and 1000. Where the ZSM-5 is a Ga ZSM-5 with Ga in or out of the zeolite framework, the preferred $\text{SiO}_2/\text{Ga}_2\text{O}_3$ mole ratio is in the range from about 10 to about 1,000.

The process described herein is generally carried out as a semi-continuous or continuous operation utilizing a fixed or moving bed catalyst system.

In accordance with the method of reforming or aromatizing of the invention a hydrocarbon feedstock is contacted under reforming or aromatization conditions with a catalyst as defined above with the catalyst having been exposed to a hydrogen atmosphere following coking as described above.

The process of the present invention can suitably be carried out under conditions which include a pressure from about 0 to about 800 psig, preferably from about 50 to about 400 psig, a liquid hourly space velocity of 0.5 to 10, preferably 0.5 to 5 and more preferably 1 to 4, a hydrogen to hydrocarbon mole ratio of 1 to 20, preferably 2 to 10. The conditions are generally adjusted so as to produce a BTX yield of about 40% on a hydrogen-free basis.

In accordance with one embodiment of the present invention the catalyst is used in the reforming operation followed by the use of a second

stage non-acidic aromatization catalyst which will increase aromatics yield. The catalyst for increasing aromatics generation may be based on an inorganic oxide support, e.g., alumina or a molecular sieve such as L-zeolite or silicalite, with an inorganic oxide binder. Preferred catalysts for increasing aromatization yield include catalysts comprising platinum on non-acidic forms of beta-zeolite, ZSM-5, silicalite and L-zeolite. Other well-known aromatization catalysts typically contain a catalytic metal, e.g., a platinum group metal such as platinum, disposed on any of a plethora of natural and man-made crystalline aluminosilicates. Other promoter metals, e.g., rhenium or tin, can also be included. The preferred catalyst for increasing aromatics yield is Pt on L-zeolite. L-zeolite suitable for this purpose can be made as set forth in U. S. Patent 4,634,518 issued January 6, 1987 to W. C. Buss and T. R. Hughes which is hereby incorporated herein by reference. A more preferred form of L-zeolite catalyst for the second stage is set forth in commonly assigned U.S. patent application Serial No. 08/151,814 of B. Mulaskey, et al, filed November 15, 1993, the disclosure of which is incorporated herein by reference.

The invention will be better understood by reference to the following experimental examples.

EXAMPLE 1: Preparation of Pt/Ga HZSM-5

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Ga ZSM-5 was prepared with a $\text{SiO}_2/\text{Ga}_2\text{O}_3$ ratio of approximately 50. The sodium salt of the Ga ZSM-5 was ion exchanged with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ in aqueous ammonia at pH 9. The catalyst was dried at 121°C and calcined at 288°C to give, Pt/Ga HZSM-5. The amounts

35

used calculate as providing 0.5% Pt by weight on Ga HZSM-5.

5 EXAMPLE 2: PARA-XYLENE SELECTIVE REFORMING OF N-OCTANE

 This example illustrates coking and hydrogen
activation procedures which provide a stabilized high
conversion and high yield catalyst which is also
10 selective for producing para-xylene at above
equilibrium concentrations. It is especially surprising
that the Pt containing catalyst can be coked to give a
high para-xylene selectivity and then hydrogen activated
to give high conversions and high aromatic yields
15 without loss of para-xylene selectivity.

 About 0.5 cc of the Pt/Ga HZSM-5 from Example
1 was placed in a down-flow micro-reactor and reduced
with hydrogen at about 510°C. Hydrogen and
n-octane were passed over the catalyst at 427°C and the
20 products were analyzed by gas chromatography using an
in-line sample valve. The results of this analysis and
other analyses taken during the run are given in Table
1. As shown in Table 1 for the sample at 427° C, the C₈
aromatics (xylenes + ethylbenzene) yield was very low
25 and the para-xylene content was approximately at
equilibrium.

 The catalyst was subjected to high temperature
coking conditions using toluene and decreasing amounts
of hydrogen. After 25 hours
30 at about 593°C with toluene and no hydrogen, the
para-xylene content of the xylenes had increased to 61%
but the toluene conversion had dropped to 11%.

 After the high temperature toluene treatment,
the xylenes from reforming n-octane at 510°C had a para-
35 xylene content of 73%, well above

equilibrium, but the feed conversion had dropped to 4%. The deactivated catalyst was hydrogen activated by turning the feed off and running hydrogen-only at 510°C for periods of 0.5 to several days. As a result of these hydrogen activation treatments, the activity was increased to give feed conversions of 70+% while the para-xylene selectivity was maintained well above equilibrium. However, under the conditions used, the activity fell rapidly over a period of a few hours after each hydrogen activation. As shown in Table 1 for the HYDROGEN ACTIVATED case, the conversion dropped from 71% to 24% in 30 hours. The catalyst activity was stabilized by hydrogen activation in combination with raising the hydrogen to feed ratio. As Table 1 shows, the conversion was stabilized for more than 100 hours at 70+% with a C₈ aromatics yield of 15-18% and a para-xylene content of 90% of the xylenes. A comparison with the fresh catalyst results in Table 1 shows that the coking and hydrogen activation process of the present invention has increased both the C₈ aromatics yield and the para-xylene content.

TABLE 1

STATUS	FRESH	TOLUENE COKING	COKED	HYDROGEN ACTIVATED	HYDROGEN STABILIZED
FEED	N-C ₈	TOLUENE	N-C ₈	N-C ₈	N-C ₈
LHSV	2	2	2	2	2
H ₂ /FEED	7.8	0	3.9	3.9	7.8
TEMP., °C	427	593	510	510	510
P, psig	50	62 80	70	70 70	85 82
RUN HOURS	100	522 546	738	1340 1370	1777 1893
%CONVERSION	100	29 11	4	71 24	70 72
%YIELD C ₈ AROMATICS	4	6.6 5	0.75	23 9	15 18
PX, % of C ₈ AROMATICS	23	25 52	61	58 69	77 77
PX, % of XYLENES	23	25 61	73	66 83	90 90

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EXAMPLE 3: COKING WITHOUT DEACTIVATION

5 This example illustrates the process where the high temperature coking is accomplished without deactivation.

About 0.5 cc of the Pt/Ga HZSM-5 from Example 1 was placed in a down-flow micro-reactor and reduced with hydrogen at about 510°C as in Example 2. The catalyst was subjected to high temperature toluene treatment at 593°C with no hydrogen in order to increase para-xylene selectivity. After about 24 hours, the toluene feed was turned off and the catalyst was held at 593°C for 64 hours with only nitrogen flowing. The high temperature toluene treatment was then continued until the para-xylene content of the C₈ aromatics had increased to 60%. The feed was changed to n-octane/hydrogen and the run was continued for a time at 593°C and then at 510°C. The analytical results for samples taken during this run are summarized in Table 2. As the results in Table 2 show, the coked catalyst gave 99% feed conversion and para-xylene concentrations substantially above equilibrium. This illustrates that controlled high temperature treatment of the catalyst with and without hydrocarbon feed can be used to achieve para-xylene selective reforming performance without loss of catalyst activity.

Table 2

STATUS	TOLUENE COKING	N ₂ TREAT	TOLUENE COKING	N-C ₈ REFORMING	
FEED	TOLUENE	NONE	TOLUENE	N-C ₈	N-C ₈
LHSV	1	0	1	1	1
H ₂ /FEED	0	0	0	8.3	8.3
TEMP., °C	593	593	593	593	510
P, psig	65 62	62	62 62	62 63	62
RUN HOURS	196 219		288 311	335 357	390
%CONVERSION	4.5 8		8.4 7	100 99	99
%YIELD C ₈ AROMATICS	1 0.7		0.4 0.5	34 28	33
PX, % of C ₈ AROMATICS	28 40		50 60	60 68	68

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EXAMPLE 4: HYDROGEN TREATMENT TO IMPROVE
AROMATICS YIELD

5 This example illustrates the use of the
hydrogen treatment to activate the catalyst for
the production of aromatics. This example is a
continuation of the catalyst test described in
10 Example 3. At about 390 hours of the run described
in Example 3, the feed was turned off and the catalyst
was treated with hydrogen for more than 60 hours.
The n-octane feed was then turned on and the test
continued. As the analytical results in Table 3 show,
15 the hydrogen treatment resulted in increased yield of
the aromatics.

Table 3

STATUS	N-C ₈ REFORMING		HYDROGEN ONLY	N-C ₈ REFORMING	
FEED	N-C ₈	N-C ₈	H ₂	N-C ₈	
LHSV	1	1		1	
H ₂ /FEED	8.3	8.3		8.3	
TEMP., °C	593	510	510	510	
P, psig	62	63	62	62	62
RUN HOURS	335	357	390	462	527
%CONVERSION	100	99	99	99.9	99.9
%YIELD C ₈ AROMATICS	34	28	33	44	44
PX, % of C ₈ AROMATICS	60	68	68	70	66
% YIELD BTX	41	30	35	49	49

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EXAMPLE 5: REFORMING A BROAD RANGE FEED

5 This example illustrates the use of the catalyst and process of the present invention to achieve para-xylene selective reforming with a broad range feed. The feed was a 149°C end point feed with the approximate composition by carbon number shown in Table 4. The aromatics content was less than 10%.

10

Table 4

15

Carbon Number	Weight Percent
C ₄ -	0.45
C ₅	1.99
C ₆	14.26
C ₇	46.93
C ₈	32.04
C ₉ +	4.35

20

The catalyst is the same one used in Examples 3 and 4. The catalyst test described in Example 4 was continued with a change from n-octane feed to the feed described in Table 4 at about 530 run hours. The test was continued for more than 100 hours with BTX yields of 42+%, C₈ aromatics yields of 18+% and para-xylene contents of 43+% of the C₈ aromatics. The results are summarized in Table 5.

30

Table 5

STATUS	BROAD RANGE FEED REFORMING	
FEED	DESCRIBED IN TABLE 4	
LHSV	1	
HYDROGEN/FEED RATIO	7.2	
TEMPERATURE, °C	510	
P, psig	62	70
RUN HOURS	532	677
WT. % BTX YIELD	45.5	42
WT. % C ₈ AROMATICS YIELD	21	18.5
PX as % of C ₈ AROMATICS	43	50

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EXAMPLE 6: PROCESS WITH ADD-ON CATALYST

5 This example illustrates the process of the
present invention when used with two catalysts in
sequence to increase aromatics yield. The catalyst test
described in Example 5 was continued with the addition
of a non-acidic Pt on L zeolite as an add-on catalyst.
The non-acidic Pt on L zeolite was prepared as was the
10 catalyst described in U.S. Patent 4,634,518 issued
January 6, 1987 to W.C. Buss and T.R. Hughes. The Pt
on L catalyst was downstream from the coked and hydrogen
activated Pt/Ga HZSM-5 of Examples 3, 4, and 5. The
feed was the same as that used in Example 5. The Pt/L
15 catalyst was held at 455°C with the Pt/Ga HZSM-5 at
510°C. As shown in Table 6, the addition of the Pt/L
catalyst resulted in an increase in the BTX yield from
the 42-45.5% shown in Table 5 to 51+% shown in Table 6.
The para-xylene content in the C₈ aromatics was also
20 maintained above equilibrium levels.

Table 6

STATUS	Dual Catalysts Pt/Ga HZSM-5 over Pt/L	
FEED	DESCRIBED IN TABLE 4	
LHSV	0.5	
HYDROGEN/FEED RATIO	7.2	
TEMPERATURE, °C	510/455 ¹	
P, psig	69	69
RUN HOURS	840	892
WT. % BTX YIELD	51.2	51.5
PX as % of C ₈ AROMATICS	34	34

(1) Pt/Ga HZSM-5 @ 510°C and Pt/L @ 455°C.

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EXAMPLE 7: DUAL CATALYST PROCESS

5 This example illustrates the present invention
when implemented with two catalysts in the same reactor
bed. A two-staged catalyst bed was prepared with the
catalyst from Example 1 as the first stage above a Pt/L-
zeolite second stage catalyst. This is similar to
10 Example 6 except that both catalysts were in the same
reactor and both catalysts were exposed to the same on-
stream history. The second stage catalyst was also
prepared as was the catalyst described in U.S. Patent
4,634,518 issued on January 6, 1987 to W.C. Buss and
T.R. Hughes. The catalysts were pretreated with
15 hydrogen at 510°C. The test was started with
hydrogen/n-octane feed. The analytical results for
samples taken during the run are summarized in Figure 1.

20 With the fresh catalysts, the feed was 100%
converted at 510°C but no xylenes were produced. The
high temperature coking of the catalysts at 593°C was
interspersed with periods of hydrogen-only treatments
for a period of time spanning more than 300 hours. The
coke buildup was accompanied by an increase in back
25 pressure. The hydrogen-only treatments helped to keep
the back pressure from becoming excessive but also may
have helped avoid excessive catalyst deactivation during
coking. After coking and hydrogen treatments, as shown
in Figure 1, the catalysts gave high feed conversions,
30 high aromatics yields, and substantially higher than
equilibrium contents of para-xylene in the C₈ aromatics.

EXAMPLE 8: DUAL CATALYST WITH BROAD RANGE FEED

5 This example illustrates the present invention
when implemented with two catalysts in the same reactor
bed and with a broad range feed. The catalyst test
described in Example 7 and Figure 1 was continued with
the broad boiling range feed described in Table 4 and
10 Example 5. Figure 2 shows the yield results after the
test run had lined out at about 700 hours. As Figure 2
shows, the catalysts and process of the present
invention gave high aromatics yields (50+% BTX and 20+%
C₈ aromatics) and higher than equilibrium levels of para-
xylene (40+%) in the C₈ aromatics. Figure 2 also shows
15 that the high yield and selectivity was maintained for
at least about 300 hours with no significant change in
performance.

20 EXAMPLE 9: DUAL CATALYST WITH N-HEPTANE FEED

This example illustrates that the catalysts
and process of the present invention does not produce
significant levels of para-xylene or other xylenes by
25 the reforming and toluene disproportionation pathway.
The low xylene yields obtained from toluene
disproportionation in Example 2 and Table 1 as well as
Example 3 and Table 2 have already shown that the
catalysts of the present invention are not suitable as
30 toluene disproportionation catalysts. The present
example reinforces this point by showing that the
catalysts and process of the present invention do not
produce xylenes to a significant extent from the
aromatization of feed components to toluene followed by
35 toluene disproportionation to xylenes and benzene.

The catalyst test in Example 8 was continued with a change of feed to n-heptane at about 1000 hours run time. As Figure 2 shows, the change to n-heptane feed resulted in a sudden severe drop in C₈ aromatics yield. More details are provided in Table 7. Table 7 gives selected characteristic results that were obtained with the three different feeds which were used in Examples 7, 8, and 9. As Table 7 shows, n-heptane gave the highest yields of toluene and the lowest yields of xylenes.

TABLE 7

STATUS	N-C ₃ REFORMING	C ₅₋₉ REFORMING	N-HEPTANE REFORMING
FEED	N-OCTANE	BROAD RANGE	N-HEPTANE
LHSV	0.5	0.5	0.5
H ₂ /FEED	8.3	7.2	7.5
TEMP., °C	510	510	510
P, psig	130	130	130
RUN HOURS	692	928	1072
% CONVERSION	98.5		98.1
% YIELD TOLUENE	6.1	23.7	39
% YIELD XYLENES	35	19.2	2.6
PX, as % of XYLENES	85.8	54.4	72.6
			73.1

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Industrial Applicability

The present invention is useful for the production of aromatics, most particularly of para-xylene. It can also produce a gasoline blending stock along with the para-xylene enriched BTX fraction.

5 While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention and the limits of the appended claims.



Claims

That which is claimed is:

1. A catalyst useful for converting a paraffinic or olefinic feed in a reforming or aromatization operation under reforming or aromatization conditions to a product which includes xylenes which are
5 enriched in para-xylene, the catalyst comprising an intermediate pore size molecular sieve support, a platinum group component and an additional component selected from the group consisting of gallium, zinc, indium, iron, tin and boron, the catalyst having an
10 activity sufficient to produce a yield of at least about 30%, on a hydrogen free basis, based on a C₆-C₈ non-aromatics portion of the feedstock, of benzene-toluene-xylenes-ethyl benzene (BTX) from a C₅-C₉ predominantly paraffinic or olefinic hydrocarbon feedstock, the C₆-C₈
15 non-aromatics portion comprising at least about 30% of the feedstock, at least about 15% of the BTX consisting of xylenes, with the xylenes being at least about 30% para-xylene.

2. A catalyst as set forth in claim 1, wherein the catalyst has been coked sufficiently to be capable of converting toluene to xylenes which are enriched in para-xylene.

3. A catalyst as set forth in claim 2, wherein following coking the catalyst has been exposed to a hydrogen containing atmosphere for a time sufficient so that it is capable of converting at least
5 30% of an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.



- 39 -

4. A catalyst as set forth in claim 3,
wherein the support is ZSM-5, ZSM-11, ZSM-12, ZSM-21,
ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23,
SSZ-25, SSZ-32, SAPO-11, SAPO-31, SAPO-41, MAPO-11 or
5 MAPO-31.

5. A catalyst as set forth in claim 4,
wherein the platinum group component is platinum in an
amount within a range from 0.1 to 5 weight percent based
on the support.

6. A catalyst as set forth in claim 5,
wherein the additional component is gallium in an amount
within a range from 0.1 to 10 weight percent based on
the support.

7. A catalyst as set forth in claim 6,
wherein the support comprises ZSM-5 having a silica to
alumina mole ratio which falls within a range from 10:1
to 1,000:1.



8. A method of producing a reforming or aromatization catalyst having an activity sufficient to convert at least 30%, based on the feed on a hydrogen free basis, of a n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5 to 10, a pressure of 0 to 800 psig and a hydrogen to hydrocarbon molar ratio within the range from 1:1 to 20:1, the products containing at least 15% xylenes, at least about 30% of the xylenes consisting of para-xylene, the method comprising:

contacting a catalyst comprising an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron with a hydrocarbon feedstock until the catalyst becomes coated with coke sufficiently so that it is capable of converting toluene by disproportionation to xylenes which are rich in para-xylene; and

exposing the coked catalyst to a hydrogen atmosphere for a time sufficient so that, following such exposure, it is capable of converting at least 30% of an n-octane feed to chemicals other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.



9. A method as set forth in claim 8, wherein the contacting step is carried out at a temperature of 500°C to 700°C, a pressure of 0 to 1,000 psig, a hydrogen to hydrocarbon mole ratio of 0 to 1 and a liquid hourly space velocity of 0.1 to 20.

10. A method as set forth in claim 9, wherein the exposing step is carried out for a time sufficient so that the catalyst, following the exposing, is capable of converting at least 30% of an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.

11. A method as set forth in claim 10, wherein the support is ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-25, SSZ-32, SAPO-11, SAPO-31, SAPO-41, MAPO-11 or MAPO-31.

12. A method as set forth in claim 11, wherein the platinum group component is platinum in an amount within a range from 0.1 to 5 weight percent based on the support.

13. A method as set forth in claim 12, wherein the additional component is gallium in an amount within a range from 0.1 to 10 weight percent based on the support.

14. A method as set forth in claim 13, wherein the support comprises ZSM-5 having a silica to alumina mole ratio which falls within a range from 10:1 to 1,000:1.



15. A method of reforming or aromatizing a C_3 - C_8 , predominantly paraffinic or olefinic hydrocarbon feedstock to produce a reformat which is enriched in para-xylene, comprising:

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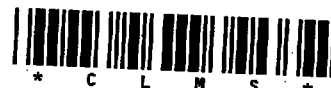
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contacting the feedstock under reforming or aromatization conditions with a para-modified catalyst comprising an intermediate pore size molecular sieve support, a platinum group component and a component selected from the group consisting of gallium, zinc, indium, iron, tin and boron to produce a hydrocarbon product, the para-modified catalyst having an activity sufficient to produce a yield of at least about 30%, on a hydrogen free basis, based on a C_6 - C_8 non-aromatics portion of the feedstock, of benzene-toluene-xylenes-ethyl benzene (BTX) from a C_3 - C_8 , predominantly paraffinic or olefinic hydrocarbon feedstock, the C_6 - C_8 non-aromatics portion comprising at least about 30% of the feedstock, at least about 15% of the BTX consisting of xylenes, with the xylenes being at least about 30% para-xylene.

16. A method as set forth in claim 15, wherein the para-modified catalyst has been coked sufficiently to be capable of converting toluene to xylenes which are enriched in para-xylene.



17. A method as set forth in claim 16, wherein following coking the para-modified catalyst has been exposed to a hydrogen containing atmosphere for a time sufficient so that it is capable of converting at
5 least 30% of an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.

18. A method as set forth in claim 17, wherein the intermediate pore size molecular sieve support is ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-25, SSZ-32, SAPO-11, SAPO-31, SAPO-41, MAPO-11 or MAPO-31.

19. A method as set forth in claim 18, wherein the platinum group component is platinum in an amount within a range from 0.1 to 5 weight percent based on the intermediate pore size molecular sieve support.

20. A method as set forth in claim 19, wherein the additional component is gallium in an amount within a range from 0.1 to 10 weight percent based on the intermediate pore size molecular sieve support.

21. A method as set forth in claim 20, wherein the intermediate pore size molecular sieve support comprises ZSM-5 having a silica to alumina mole ratio which falls within a range from 10:1 to 1,000:1.



22. A method as set forth in claim 15, further including:

separating the reformat into a BTX containing fraction and a BTX-free raffinate fraction.

23. A method as set forth in claim 15, wherein the feedstock contains no more than about 30% aromatics.

5 24. A method as set forth in claim 15, further including:

 contacting the hydrocarbon product in a
 subsequent aromatization stage under reforming
 or aromatization conditions with an
10 aromatization catalyst comprising a platinum
 group component on a non-acidic inorganic
 oxide support.

25. A method as set forth in claim 24, wherein the para-modified catalyst has been coked sufficiently to be capable of converting toluene to xylenes which are enriched in para-xylene.

26. A method as set forth in claim 25, wherein following coking the para-modified catalyst has been exposed to a hydrogen containing atmosphere for a time sufficient so that it is capable of converting at
5 least 30% of an n-octane feed to products other than n-octane at a temperature of 500°C, a liquid hourly space velocity of 0.5, a pressure of 75 psig and a hydrogen to hydrocarbon molar ratio of 10:1.



27. A method as set forth in claim 26,
wherein the intermediate pore size molecular sieve
support is ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-22,
ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23,
5 SSZ-25, SSZ-32, SAPO-11, SAPO-31, SAPO-41, MAPO-11
or MAPO-31.

28. A method as set forth in claim 27,
wherein the platinum group component is platinum in an
amount within a range from 0.1 to 5 weight percent based
on the intermediate pore size molecular sieve support.

29. A method as set forth in claim 28,
wherein the additional component is gallium in an amount
within a range from 0.1 to 10 weight percent based on
the intermediate pore size molecular sieve support.

30. A method as set forth in claim 29,
wherein the intermediate pore size molecular sieve
support comprises ZSM-5 having a silica to alumina mole
ratio which falls within a range from 10:1 to 1,000:1.

31. A method as set forth in claim 24,
further including:

separating the reformat into a BTX containing
fraction and a BTX-free raffinate fraction.

32. A method as set forth in claim 24,
wherein the feedstock contains no more than about 30%
aromatics.

PARA-XYLENE SELECTIVE REFORMING/AROMATIZATION

Abstract Of The Disclosure

5 An intermediate pore size molecular sieve
supported catalyst includes a platinum group component
and a gallium, zinc, indium, iron, tin or boron
component. It is used for reforming and aromatization
during which it produces a para-xylene enriched product.
10 It comprises an intermediate pore size molecular sieve
support, a platinum group component and a component
selected from the group consisting of gallium, zinc,
indium, iron, tin or boron. One form of the catalyst is
first coked and is then contacted with hydrogen. The
15 catalyst is useful in reforming and aromatizing
operations.

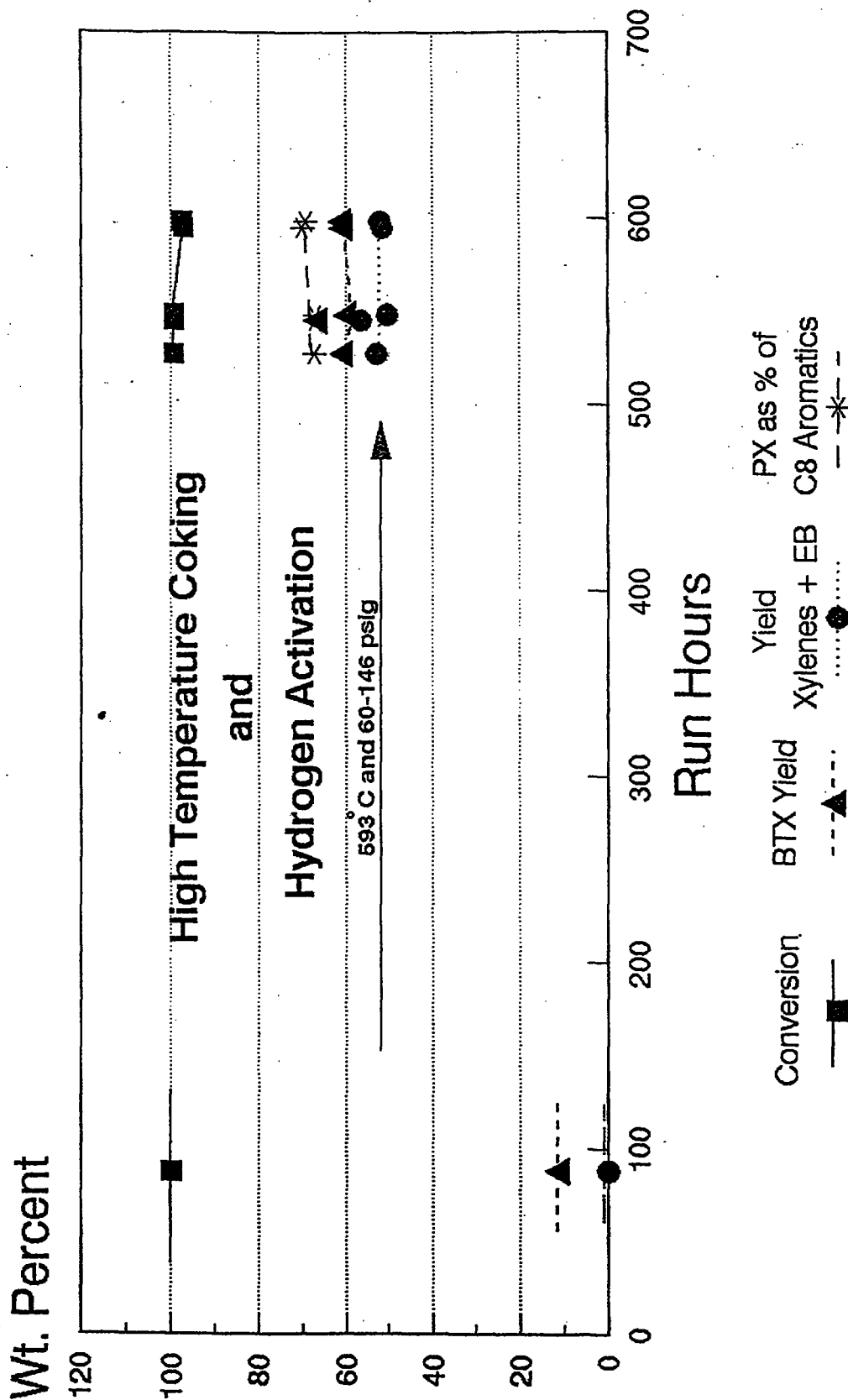
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FIGURE 1: REFORMING N-OCTANE

Dual Catalyst: Pt/Ga HZSM-5 plus Pt/L
510°C, 50-130 psig, LHSV=1, H₂/Feed = 8



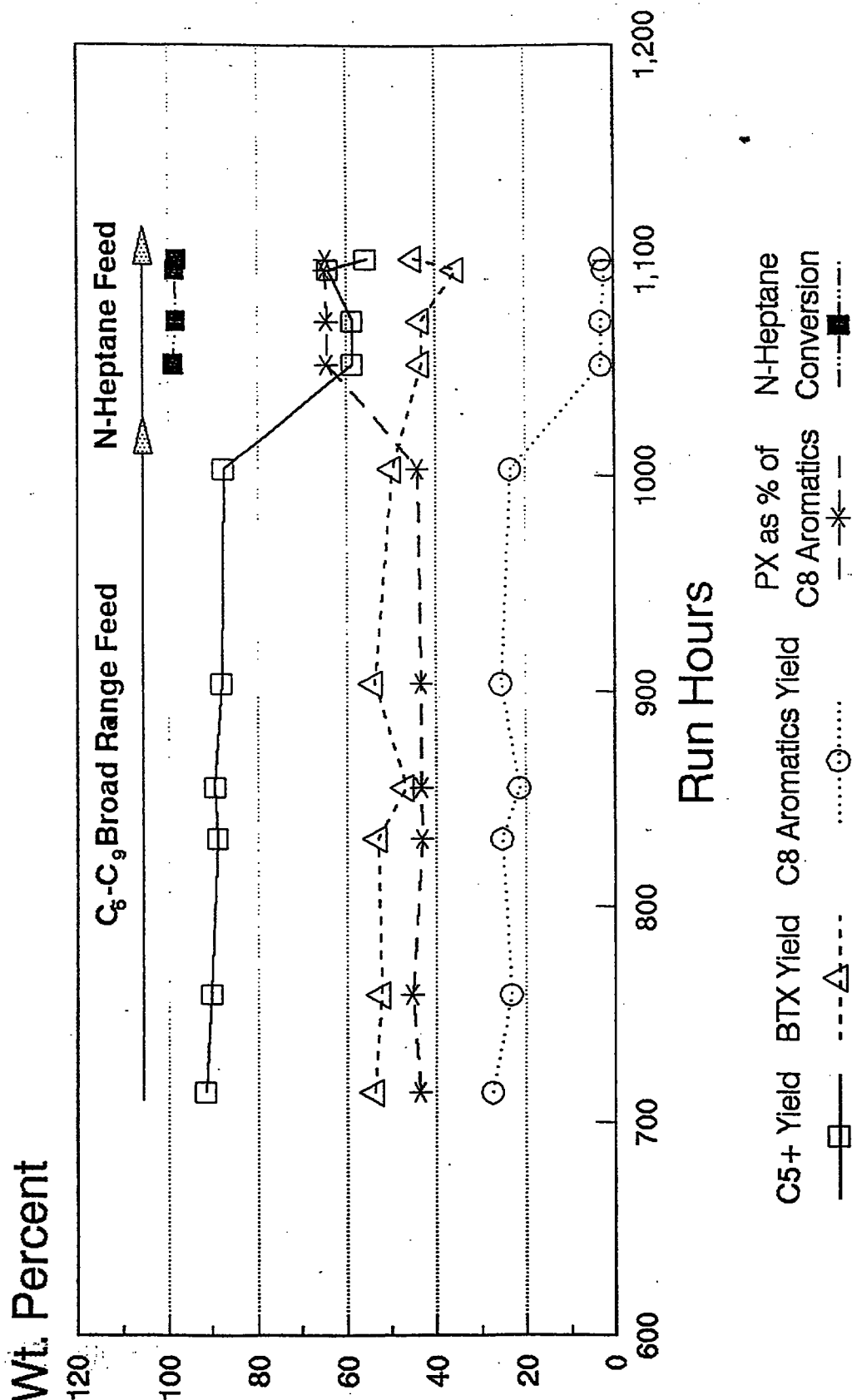
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FIGURE 2: REFORMING A BROAD RANGE FEED AND N-HEPTANE

Dual Catalyst: Pt/Ga HZSM-5 plus Pt/L
 510°C, 130 psig, LHSV = 0.5, H₂/FEED = 8



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TABLE 1

STATUS	FRESH	TOLUENE COKING	COKED	HYDROGEN ACTIVATED	HYDROGEN STABILIZED
FEED	N-C ₈	TOLUENE	N-C ₈	N-C ₈	N-C ₈
LHSV	2	2	2	2	2
H ₂ /FEED	7.8	0	3.9	3.9	7.8
TEMP., °C	427	593	510	510	510
P, psig	50	62 80	70	70 70	85 82
RUN HOURS	100	522 546	738	1340 1370	1777 1893
%CONVERSION	100	29 11	4	71 24	70 72
%YIELD C ₈ AROMATICS	4	6.6 5	0.75	23 9	15 18
PX, % of C ₈ AROMATICS	23	25 52	61	58 69	77 77
PX, % of XYLENES	23	25 61	73	66 83	90 90

Table 2

STATUS	TOLUENE COKING	N ₂ TREAT	TOLUENE COKING	N-C ₈ REFORMING
FEED	TOLUENE	NONE	TOLUENE	N-C ₈
LHSV	1	0	1	1
H ₂ /FEED	0	0	0	8.3
TEMP., °C	593	593	593	510
P, psig	65 62	62	62 62	62 63
RUN HOURS	196 219		288 311	335 357 390
%CONVERSION	4.5 8		8.4 7	100 99 99
%YIELD C ₈ AROMATICS	1 0.7		0.4 0.5	34 28 33
PX, % of C ₈ AROMATICS	28 40		50 60	60 68 68

Table 3

STATUS	N-C ₈ REFORMING		HYDROGEN ONLY	N-C ₈ REFORMING	
	N-C ₈	N-C ₈		N-C ₈	N-C ₈
FEED			H ₂		
LHSV	1	1			1
H ₂ /FEED	8.3	8.3			8.3
TEMP., °C	593	510	510		510
P, psig	62	63	62	62	62
RUN HOURS	335	357		462	527
%CONVERSION	100	99		99.9	99.9
%YIELD C ₈ AROMATICS	34	28		44	44
PX, % of C ₈ AROMATICS	60	68		70	66
% YIELD BTX	41	30		49	49

Table 5

STATUS	BROAD RANGE FEED REFORMING	
FEED	DESCRIBED IN TABLE 4	
LHSV	1	
HYDROGEN/FEED RATIO	7.2	
TEMPERATURE, °C	510	
P, psig	62	70
RUN HOURS	532	677
WT. % BTX YIELD	45.5	42
WT. % C ₈ AROMATICS YIELD	21	18.5
PX as % of C ₈ AROMATICS	43	50

Table 6

STATUS	Dual Catalysts Pt/Ga HZSM-5 over Pt/L	
FEED	DESCRIBED IN TABLE 4	
LHSV	0.5	
HYDROGEN/FEED RATIO	7.2	
TEMPERATURE, °C	510/455 ¹	
P, psig	69	69
RUN HOURS	840	892
WT. % BTX YIELD	51.2	51.5
PX as % of C ₈ AROMATICS	34	34

(1) Pt/Ga HZSM-5 @ 510°C and Pt/L @ 455°C.

TABLE 7

STATUS	N-C ₈ REFORMING	C ₅₋₉ REFORMING	N-HEPTANE REFORMING
FEED	N-OCTANE	BROAD RANGE	N-HEPTANE
LHSV	0.5	0.5	0.5
H ₂ /FEED	8.3	7.2	7.5
TEMP., °C	510	510	510
P, psig	130	130	130
RUN HOURS	692	928	1072
% CONVERSION	98.5		98.1
% YIELD TOLUENE	6.1	23.7	41
% YIELD XYLENES	35	19.2	2.64
PX, as % of XYLENES	85.8	54.4	72.6
			73.1

PARA-XYLENE SELECTIVE REFORMING/AROMATIZATION

Abstract Of The Disclosure

5 An intermediate pore size molecular sieve
supported catalyst includes a platinum group component
and a gallium, zinc, indium, iron, tin or boron
component. It is used for reforming and aromatization
during which it produces a para-xylene enriched product.
10 It comprises an intermediate pore size molecular sieve
support, a platinum group component and a component
selected from the group consisting of gallium, zinc,
indium, iron, tin or boron. One form of the catalyst is
first coked and is then contacted with hydrogen. The
15 catalyst is useful in reforming and aromatizing
operations..

Figure 2

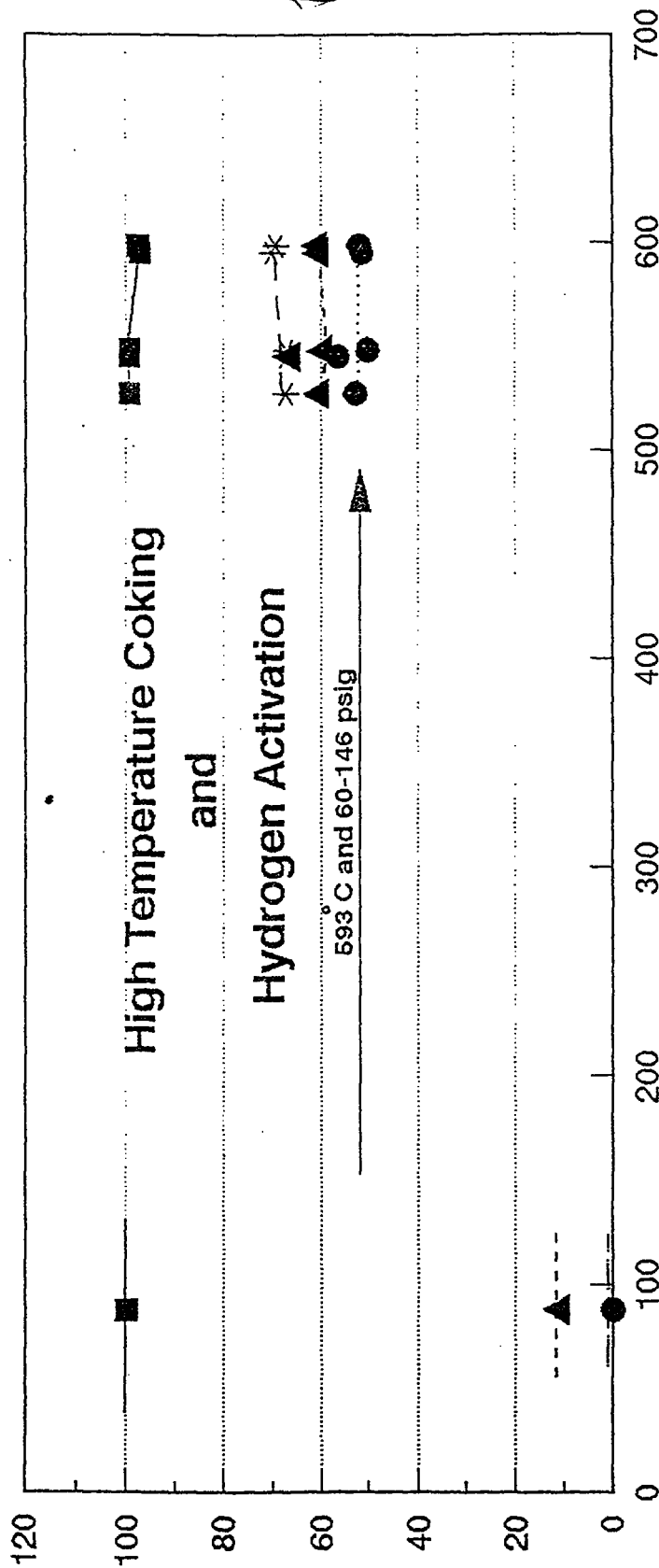
REPLACEMENT SHEET

01 MAR 1996

FIGURE 1: REFORMING N-OCTANE

Dual Catalyst: Pt/Ga HZSM-5 plus Pt/L
510°C, 50-130 psig, LHSV=1, H₂/Feed = 8

Wt. Percent



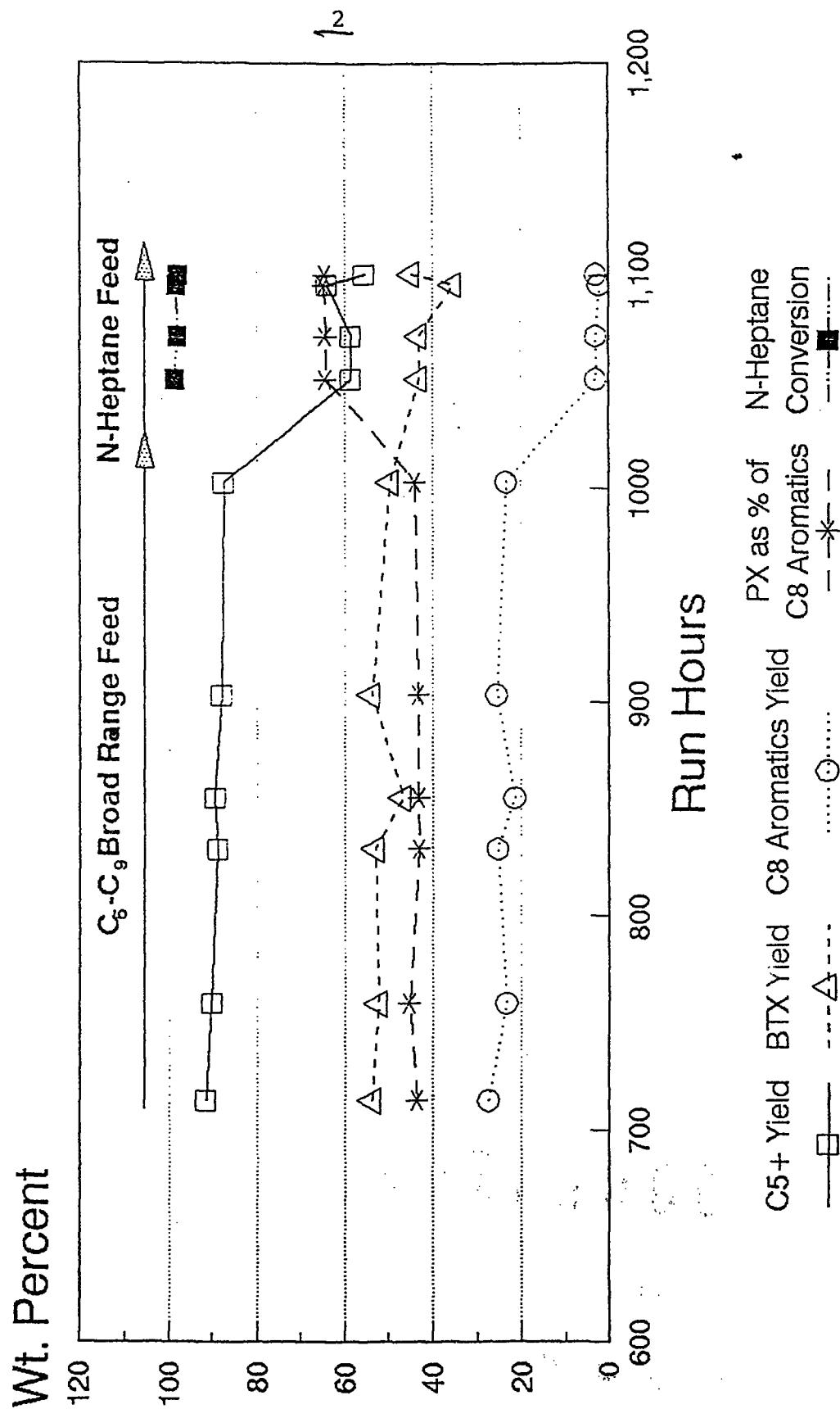
REPLACEMENT SHEET

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FIGURE 2: REFORMING A BROAD RANGE FEED AND N-HEPTANE

Dual Catalyst: Pt/Ga HZSM-5 plus Pt/L

510°C, 130 psig, LHSV = 0.5, H₂/FEED = 8



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