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(54) Title: LOW PRESSURE HYDRODEALKYLATION OF ETHYLBENZENE AND XYLENE ISOMERIZATION

(57) Abstract

A new process for the hydrodealkylation of ethylbenzene and the isomerization of xylenes at low pressure and at a low hydrogen to ethylbenzene mole ratio as well as a low hydrogen to hydrocarbon feed mole ratio using a catalyst comprising (a) HZSM-5 having a particle size less than 1.0 microns, and (b) a Group VIII metal such as platinum.

1   LOW PRESSURE HYDRODEALKYLATION OF ETHYLBENZENE

2   AND XYLENE ISOMERIZATION

3   FIELD OF THE INVENTION

4   The present invention relates to a catalyst and process for hydrodealkylating

5   ethylbenzene and isomerizing xylenes. Preferably, the ethylbenzene and xylenes are

6   in a C_8 aromatics stream lean in paraxylene.

7   BACKGROUND OF THE INVENTION

8   The xylene isomers metaxylene, orthoxylene and, in particular, paraxylene, are

9   important chemical intermediates. Orthoxylene is oxidized to make phthalic anhydride

10   which is used to make phthalate based plasticizers among other things. Metaxylene is

11   oxidized to make isophthalic acid which is used in unsaturated polyester resins.

12   However, paraxylene has by far the largest market of the three isomers. The largest

13   use of paraxylene is in its oxidation to make terephthalic acid. Terephthalic acid in

14   turn is used to make polymers such as polytrimethyleneterephthalate,

15   polybutyleneterephthalate (PBT), and polyethyleneterephthalate (PET). PET is made

16   via condensation polymerization of terephthalic acid with ethylene glycol.

17   PET is one of the largest volume polymers in the world. It is used to make PET

18   plastics (e.g., two liter PET bottles). It is also used to make polyester fiber which, in

19   turn, is used to make clothes and other fabrics. Polyester fiber is used both as a

20   homofiber, as well as a blended fiber, such as a blend with cotton. Given the large

21   market for PET plastics and fibers, there is a substantial demand for high purity

22   paraxylene. The demand for paraxylene is several times larger than the demand for

23   ortho and metaxylene. The demand for paraxylene is also larger than the amount of

24   paraxylene in the xylenes recovered as a by-product, such as the xylenes recovered

1   from reformate (from catalytic reformers) and from pygas (from high temperature

2   cracking to make light olefins).

3   Because the demand for paraxylene is so much larger than the demand for the other

4   xylene isomers and is larger even than the supply of paraxylene in xylenes recovered

5   as a by-product, it has been found that isomerization of xylene isomers is desirable to

6   increase the amount of paraxylene production. Paraxylene is typically produced by

7   reforming or aromatizing a wide boiling range naphtha in a reformer, for example, a

8   CCR (Continuous Catalytic Reformer), and then separating by distillation a C_8

9   aromatics rich fraction from the reformer effluent. This C_8 fraction comprises near

10   equilibrium amounts of ethylbenzene and the three xylene isomers, namely, para-,

11   meta- and ortho-xylene. The paraxylene in this C_8 aromatics fraction is separated by

12   either crystallization or adsorption. Rather than simply returning the paraxylene

13   depleted C_8 aromatics stream to the refinery for a relatively low value use such as

14   gasoline blending, the C_8 aromatics stream which is depleted in paraxylene is typically

15   further processed by passing it over a xylene isomerization catalyst in a xylenes

16   isomerization unit. The resulting C_8 aromatics stream, which now has an

17   approximately equilibrium concentration of xylenes, i.e., a higher concentration of

18   paraxylene, is recycled to the paraxylene separation process.

19   The xylene isomerization unit typically serves at least two functions. First, it

20   re-equilibrates the xylenes portion of the stream. Thus, in effect, it is creating

21   paraxylene from the other xylene isomers. Second, it transalkylates or

22   hydrodealkylates the ethylbenzene to facilitate its removal from the C_8 aromatics

23   fraction. Since ethylbenzene boils in the same range as the xylene isomers, it is not

24   economic to recover/remove the ethylbenzene by distillation, hence it is included in

25   the C_8 aromatics fraction that is fed to the paraxylene separation process.

26   Ethylbenzene is in general an inert from a para-xylene production standpoint, except

27   for those para-xylene production complexes which utilize a xylene isomerization

28   process where the ethylbenzene is converted to xylenes. However, as pointed out

1   earlier, such a process is limited in its ethylbenzene conversion by C_8 aromatics

2   equilibrium. Therefore, for those cases where ethylbenzene is an inert, it is highly

3   desirable to remove as much ethylbenzene as possible per pass so that it does not

4   accumulate in the recycle loop. If that were to occur, a bleed stream out of the para-

5   xylene production loop would be necessary which would reduce para-xylene

6   production. Thus, a critical function of the isomerization plant is to react-out the

7   ethylbenzene by either hydrodealkylation or transalkylation/disproportionation

8   depending on the type of isomerization process.

9   Current xylene isomerization technology is based on two types of processes, high

10 pressure processes and a low pressure process. Furthermore, within the high pressure

11 processes, there are two types of such processes. U.S. Pat. No. 4,482,773 and U.S.

12 Pat. No. 4,899,011 are two references dealing with one type of the high pressure

13 process, usually carried out at 150 psig and higher and in the presence of hydrogen.

14 U.S. Pat. No. 4,584,423 is a reference dealing with low pressure isomerization,

15 usually carried out at less than 150 psig, for example, between about 25 and 100 psig

16 and in the absence of hydrogen.

17 In the '773 and '011 high pressure processes, a C_8 aromatics-rich hydrocarbon feed is

18 contacted with a catalyst containing a ZSM-5 zeolite. Xylene isomerization is carried

19 out simultaneously with ethylbenzene hydrodealkylation to benzene and ethane. The

20 hydrogen/hydrocarbon feed mole ratio is between 2/1 and 4/1. In both these patents,

21 the objective is to achieve high levels of ethylbenzene conversion to isomerize the

22 xylene to achieve a higher content of paraxylene, preferably an equilibrium content of

23 paraxylene and to have low xylene losses. In the '773 process, ethylbenzene

24 conversion levels are about 60% and xylene losses are about 2% yielding an

25 ethylbenzene conversion/xylene loss ratio of about 30/1. Similar values are achieved

26 with the '011 high pressure process, but at ethylbenzene conversions of about 70%.

27 For both these high pressure processes, the catalyst system is very xylene selective.

1   In U.S. Pat. No. 4,482,773, the catalyst used comprises platinum and magnesium on a

2   ZSM-5 zeolite. The preferred catalyst is an HZSM-5 (H meaning that the ZSM-5 is

3   predominately in the hydrogen form) with a preferred crystal size of 1-6 microns. The

4   examples in U.S. Pat. No. 4,482,773 disclose a H_2/HC feed mole ratio of 2/1 or

5   higher.

6   The high pressure process of U.S. Pat. No. 4,899,011 is similar to the '773 process but

7   uses a dual catalyst bed system. The objective is to hydrodealkylate ethylbenzene in

8   the first catalyst layer and complete the isomerization of xylenes in the second layer.

9   The catalyst for both layers is a Pt containing ZSM-5, without any Group IIA metal

10   such as Mg. The Pt ranges from 0.05-10 wt. %. The crystal size of the first layer is

11   1 micron minimum compared to 0.1 micron maximum for the second layer. In

12   addition, the top layer is a more acidic ZSM-5 than the second layer. Operating

13   conditions for the '011 process are 400-1000°F, 0-1000 psig, 0.5-100 WHSV, and a

14   H_2/HC feed mole ratio of 0.5/1 to 10/1.

15   The catalysts for both U.S. Pat. No. 4,482,773 and U.S. Pat. No. 4,899,011 have good

16   xylene isomerization activity as determined by the Paraxylene Approach To

17   Equilibrium (PXAPE) which reaches values of 100-103%. A PXAPE of 100%

18   indicates that the paraxylene concentration on a xylene basis is at equilibrium. The

19   catalyst of both processes is based on ZSM-5. In the case of the '773 process, the

20   catalyst contains Pt and possibly Mg. The catalyst has a silica/alumina ratio of about

21   50/1 to 100/1 and a crystal size of 1-6 microns. In the case of the '011 process, the

22   catalyst bed consists of two catalyst layers, each of which contains Pt. Catalyst crystal

23   size and acidity differ with the top catalyst having a crystal size of 2-4 microns and

24   the bottom layer having a crystal size of 0.02-0.05 microns. In addition, as mentioned

25   above, the top layer is more acidic than the bottom layer.

26   It should be noted that within the high pressure xylene isomerization process

27   technology, there is a sub-type of process where the objective is to eliminate the

1　ethylbenzene by converting the ethylbenzene to xylenes. However, high levels of

2　ethylbenzene conversion as in the '773 and '011 patents are not achieved with this

3　type of process, because the ethylbenzene concentration is limited by the equilibrium

4　concentration on a C_8 aromatics basis.

5　In addition to U.S. Pat. No. 4,899,011 and U.S. Pat. No. 4,482,773 discussed above,

6　two other patents of interest are U.S. Pat. No. 4,467,129, issued August 21, 1984 to

7　Iwayama et al., and U.S. Pat. No. 4,899,010, issued February 6, 1990 to Amelse et al.

8　U.S. Pat. No. 4,467,129 is very similar to the '733 and '011 processes, in that

9　ethylbenzene is converted by hydrodealkylation and uses a mixture of mordenite and a

10　ZSM-5 which contains rhenium. A ZSM-5 containing Mg and Re is disclosed.

11　Platinum is not a catalyst component. The process operates at 572-1112°F, a pressure

12　of 0-1370 psig, and a H_2/HC feed mole ratio of 1-50/1. The examples show a

13　temperature of ~700°F, a pressure of 165 psig, and a H_2/HC feed mole ratio of 4/1.

14　We estimate the WHSV at 3.5.

15　U.S. Pat. No. 4,899,010 is also an ethylbenzene hydrodealkylation/xylene

16　isomerization process. It is based on the hydrogen form of a borosilicate equivalent of

17　ZSM-5 known as AMS-1B. The catalyst contains 0.1-1.0 wt. % Pt. Operating

18　conditions are 700-1000°F, 0-100 psig, and a H_2/HC feed mole ratio of 0.25-5.0.

19　Ethylbenzene conversions are about 25-28% and the ethylbenzene conversion/xylene

20　loss ratio is about 29.

21　Other patents of interest are U.S. Pat. Numbers 3,856,872; 4,098,836; and 4,152,263

22　which are discussed below.

23　U.S. Patent No. 3,856,872 to Morrison utilizes a ZSM-5 catalyst containing a

24　Group VIII metal, preferably nickel. Morrison operates at high pressure (150 to 300

25　psig) and a high hydrogen to hydrocarbon ratio of 6.5.

1   U.S. Patent No. 4,098,836 to Dwyer provides an improved catalyst for xylenes

2   isomerization comprising a zeolite such as ZSM-5 in combination with a group VIII

3   metal present in minimum amount of 2.0 percent by weight of said zeolite. The group

4   VIII metals exemplified are nickel, iron, and/or cobalt. Possible operating conditions

5   disclosed by Dwyer include a hydrogen to hydrocarbon (H_2 to HC) mole ratio of from

6   about 0.1 to about 100 and a pressure of from about 50 psig to about 500 psig.

7   Examples in the patent are limited to a H_2 to HC mole ratio of 1 and pressures of

8   about 200 psig (pressures given in the examples range from 183 to 214 psig).

9   U. S. Patent No. 4,152,363 to Tabak and Morrison is another xylenes isomerization

10   patent which discloses a catalyst that can comprise a ZSM-5 zeolite and a group VIII

11   metal. '363 teaches operating conditions which comprise a pressure from about 20 to

12   about 500 psig and a H_2 to HC mole ratio of about 1 to 10.

13   In the low pressure xylene isomerization process, which operates without any

14   hydrogen present, ethylbenzene conversion is achieved by the disproportionation of

15   ethylbenzene. The products of this disproportionation reaction are benzene and

16   di-ethylbenzene, a C_{10} aromatic. Ethylbenzene (EB) is also converted by another

17   reaction, namely, by transalkylation with the xylenes. This latter reaction produces

18   benzene and di-methyl-ethylbenzene, also a C_{10} aromatic. This reaction with xylenes

19   results in an undesirable loss of xylenes. Another reaction mechanism which

20   contributes to xylene loss is the disproportionation of xylenes to produce toluene and

21   trimethylbenzenes, a C_9 aromatic. All these reactions are a function of the catalyst

22   acidity. Operating conditions are such as to achieve ethylbenzene conversions of

23   about 25-40%. However, the xylene losses are high, on the order of 2.5-4.0%,

24   resulting in an ethylbenzene conversion/xylene loss ratio of 10/1. Thus, at 40%

25   ethylbenzene conversion, the xylene losses are 4%. Furthermore, high levels of

26   ethylbenzene conversion, in the range of 50-70% are not practical as the temperature

27   required to achieve these levels of ethylbenzene conversion would be quite high. At

28   70% ethylbenzene conversion, the temperature required is about 60-70°F higher than

1   that required to achieve 50% ethylbenzene conversion. In addition, the coking rate

2   would also be substantially higher due to the higher operating temperature and higher

3   level of ethylbenzene conversion. The net effect of operating at higher ethylbenzene

4   conversion is a substantial reduction in the catalyst life.

5   One key goal of xylene isomerization catalyst development efforts has been to reduce

6   xylene losses at constant ethylbenzene conversion, or to achieve higher ethylbenzene

7   conversions while reducing the xylene losses.

8   U.S. Pat. No. 4,584,423, which describes a low pressure isomerization process,

9   discloses that a Mg/ZSM-5 extrudate resulted in a 40% reduction in xylene loss when

10   used in low pressure isomerization, and a Zn/ZSM-5 extrudate resulted in a 30%

11   reduction in xylene loss when used in low pressure isomerization operating at 25%

12   ethylbenzene conversion. However, the operating temperature for the reaction zone

13   was higher relative to the base case using ZSM-5 catalyst. Operation to achieve 50%

14   ethylbenzene conversion would have required even higher operating temperatures.

15   From a catalyst stability standpoint, the high pressure processes which operate in the

16   presence of hydrogen have catalyst systems which are an order of magnitude more

17   stable than the low pressure process which operates in the absence of hydrogen. For

18   high pressure processes, catalyst stability is believed enhanced by using a catalyst

19   which contains a hydrogenation/dehydrogenation metal component, such as for

20   example platinum, palladium, or nickel, and by using a high hydrogen partial

21   pressure. The high hydrogen partial pressure is achieved by combining a high

22   system/process pressure with a high hydrogen/hydrocarbon feed mole ratio, for

23   example, 4/1. This is equivalent to a hydrogen concentration of approximately

24   80 mole %.

25   Accordingly, in a low pressure process, it would be desirable to achieve the

26   performance parameters of the high pressure isomerization processes and achieve high

1   levels of ethylbenzene conversion, while simultaneously achieving xylene

2   isomerization and very low xylene losses, and achieving high stability for the catalyst.

3   SUMMARY OF THE INVENTION

4   According to the present invention, a process is provided for hydrodealkylation of

5   ethylbenzene and isomerization of xylenes. The process comprises contacting, in a

6   reaction zone, a hydrocarbon feed containing ethylbenzene and xylenes, with a

7   catalyst comprising ZSM-5, a Group VIII metal; and wherein the paraxylene content

8   of the xylenes in the feed is less than an equilibrium amount, the contacting is carried

9   out in the presence of gaseous hydrogen, and the ZSM-5 has a crystal size of between

10   0.2 and 0.9 microns; to thereby hydrodealkylate ethylbenzene to produce benzene and

11   isomerize xylenes to produce paraxylene.

12   Preferred reaction conditions, in the reaction zone of the present invention, include a

13   temperature of 500°F to 1000°F, more preferably 600°F to 900°F, and still more

14   preferably 700°F to 900°F.

15   The reaction zone pressure is below 200 psig, preferably 0 to 150 psig, more

16   preferably below 125 psig, and still more preferably below 90 psig for example, 25 to

17   90 psig. Particularly preferred pressure is 10 to 80 psig for the reaction zone of the

18   present invention. An advantage of the present invention is achievement of high

19   ethylbenzene conversion, excellent xylene isomerization and surprisingly low xylene

20   losses at low pressure. A further advantage of the present invention is that the catalyst

21   exhibits high xylene isomerization activity as evidenced by an initial Paraxylene

22   Approach To Equilibrium (PXATE) of 100+%, as well as high xylene isomerization

23   stability. This latter key catalyst quality is evidenced by a very minor decline in the

24   PXATE with time. This stability of the PXATE allows for long and useful catalyst

25   life.

1   According to an alternate embodiment of the present invention, a particularly

2   preferred low pressure in the reaction zone is below 40 psig, and a still more preferred

3   pressure is below 35 psig.

4   The weight hourly space velocity based on the zeolite (WHSVZ), preferably is 2 to

5   20, more preferably 3 to 15, still more preferably 4 to 10, and most preferably 6 to 8.

6   Preferably, the feed to the reaction zone is a hydrocarbon stream comprising mainly

7   C_8 hydrocarbons, containing ethylbenzene, and a mixture of xylenes that is below

8   equilibrium in paraxylene content. The hydrogen to ethylbenzene mole ratio in the

9   feed is 0.3 to 15, preferably 0.7 to 15, and more preferably 1.0 to 11. Particularly

10   preferred hydrogen to ethylbenzene mole ratios are between 1.0 and 7.0, and most

11   preferably between 1.0 and 3.0 for the feed to the reaction zone of the present

12   invention.

13   The Group VIII metal of the catalyst used in the reaction zone of the process of the

14   present invention preferably is platinum. Preferably, the ZSM-5 component used to

15   make the catalyst is predominantly in the hydrogen form.

16   Among other factors, the present invention is based on our finding that when

17   combining use of:

18   (a)   a ZSM-5 based catalyst having a small ZSM-5 crystal size less than

19   0.9 microns, and associated with a Group VIII metal such as platinum with

20   (b)   low pressure, and

21   (c)   reaction conditions including the presence of low concentrations of gaseous

22   hydrogen,

1   a surprisingly high ethylbenzene conversion is achieved in the reaction zone, while

2   also achieving low xylene losses and excellent xylene isomerization activity, i.e. the

3   ability of the catalyst to isomerize the xylenes.

4   Surprisingly, we have also found that excellent xylene isomerization activity, as

5   evidenced by a PXATE of 100+%, and excellent xylene isomerization stability as

6   evidenced by a minor decline in the PXATE with time, can be maintained with the

7   catalyst of the present invention when operating at low pressure and with a low

8   hydrogen to EB mole ratio and while achieving high EB conversion at surprisingly

9   low xylene losses.

10   While others have sought to achieve similar results by the addition of various metals

11   and in particular alkaline earth metals, or by various catalyst treatments, such as

12   sulfiding, no such additives or treatments are needed for the catalyst of the invention.

13   Thus a further advantage of the catalyst of the invention is that the manufacture of the

14   catalyst is substantially simplified resulting in a lower manufacturing cost.

15   Further, we have found that due to the relatively small amount of hydrogen needed to

16   facilitate the hydrodealkylation reaction in the process of the present invention, in

17   accordance with a preferred embodiment of the present invention, recycle of unused

18   hydrogen to the reaction zone is not required. Not having to recycle hydrogen

19   simplifies the process and allows the process to be performed with less equipment and

20   a lower cost of operation. In particular, according to preferred embodiments, this

21   invention eliminates the requirement for a recycle compressor in the process.

22   Also, the present invention allows the use of relatively low pressure in the reaction

23   zone. Accordingly, the reactors and associated piping and equipment do not have to

24   be built to withstand high pressures required when using prior art processes.

1   Another advantage we have found resulting from the present invention is that the low

2   pressure isomerization process, which in the past could not utilize the

3   hydrodealkylation type process for the removal of ethylbenzene from the C_8 aromatics

4   and paraffins stream, can now be retrofitted to take advantage of this more efficient

5   process. Such older low pressure isomerization plants, still in use today, were built to

6   operate at relatively low pressures and without hydrogen. They could not be

7   economically retrofitted to accommodate prior art hydrodealkylation processes, as

8   these require high pressures in excess of 150 psig, as well as large volumes of

9   hydrogen and the ability to recycle the hydrogen.

10   Still another advantage of the present invention is that, in accordance with a preferred

11   embodiment, effective removal of a portion of the C_8 paraffins present in the feed to

12   the hydrodealkylation/isomerization reaction zone is achieved by hydrocracking such

13   paraffins to lighter paraffins, which lighter paraffins are easily removed from the C_8

14   aromatics. Preferably, at least 15%, more preferably at least 20% of the C_8 paraffins

15   are effectively removed in this manner. This is of particular advantage in paraxylene

16   production processes that utilize a feed comprising unextracted, predominately C_8

17   hydrocarbons feed containing both aromatics and nonaromatics (paraffins) from a

18   high octane catalytic reformer. Such unextracted reformate can include several

19   percent nonaromatics. These nonaromatics may build up in the paraxylene processing

20   loop requiring a bleed stream to control their concentration, unless conversion is

21   achieved in the xylene isomerization step.

22   Still a further advantage of the present invention is that it minimizes the system

23   pressure and the amount of hydrogen, expressed in terms of the hydrogen to

24   ethylbenzene mole ratio, needed for the hydrodealkylation reaction. Hydrogen is a

25   valuable and expensive commodity in a refinery or chemical complex. In the present

26   invention, minimal hydrogen is required. In addition, the hydrogen required

27   preferably is used at a relatively low pressure, allowing the hydrogen from another

28   higher pressure unit [such as from a conventional reformer using a bifunctional

1   (acidic) reforming catalyst, or AROMAX® type reformer using a monofunctional

2   (nonacidic) type catalyst] to be used in a "stepped" arrangement. Such a "stepped"

3   arrangement adds to the cost savings benefits of this invention.

4   Preferred Group VIII hydrogenation metal components for the catalyst used in the

5   process of the present invention include platinum, palladium, and nickel. Platinum is

6   particularly preferred as the hydrogenation metal in the catalyst used in the present

7   invention. Preferably, the amount of hydrogenation metal is between 0.05 and

8   20 wt. %, more preferably between 0.05 and 10 wt. %, and still more preferably

9   between 0.075 and 8, based on the weight of zeolite in the catalyst. For the

10   particularly preferred hydrogenation metal platinum, the most preferred range is 0.075

11   to 0.5 wt. %.

12   We have found that the predominantly hydrogen form of the ZSM-5 and the careful

13   control of the silica to alumina ratio in the catalyst are particularly advantageous in

14   achieving a moderated acidity and pore constraint catalyst for use in the process of the

15   present invention.

16   DETAILED DESCRIPTION OF THE INVENTION

17   According to the present invention, a catalyst and process are provided for achieving

18   high levels of ethylbenzene conversion, xylene isomerization and low xylene losses.

19   The present invention is particularly useful in a commercial scale ethylbenzene

20   hydrodealkylation/ xylene isomerization process. Such a process is often referred to

21   simply as a xylenes isomerization process. For the purposes of this invention a

22   commercial scale process for the hydrodealkylation of ethylbenzene and the

23   isomerization of xylenes has a hydrocarbon feed rate of at least 100 bbls per day,

24   preferably at least 500 bbls per day, and more preferably at least 1000 bbls per day.

1 Preferably, the catalyst comprises a small crystal size ZSM-5 containing a Group VIII

2 metal (e.g., platinum). Preferred small crystal size ZSM-5 of the catalyst used in the

3 present invention is discussed herein below, as is preferred silica to alumina ratio.

4 In a particularly preferred catalyst, the Pt content is 0.075 to 0.5 wt. %.

5 In accordance with the present invention, the process is operated at low pressure, and

6 preferably with a low flow of hydrogen. The low flow of hydrogen may be referred to

7 as "trickle flow". Preferably, the trickle flow is once-through, that is, with no recycle

8 hydrogen.

9 Ethylbenzene is converted by hydrodealkylation, preferably to benzene and ethane.

10 This is in contrast to prior art low pressure processes where the EB is converted by

11 disproportionation which is accompanied by high xylene losses and formation of

12 substantial amounts of heavy material such as C_9 aromatics and heavier.

13 The xylene losses in accordance with the process provided by the present invention

14 are substantially reduced relative to prior low pressure processes. Also, in the process

15 of the present invention, a high degree of xylene isomerization to paraxylene is

16 achieved.

17 In the process of the invention, the xylenes in the feed, which contain paraxylene on a

18 xylene basis in an amount which is less than that at thermal equilibrium on a xylene

19 basis, are converted (or isomerized) such that in the effluent from the isomerization

20 reaction zone, the paraxylene content on a xylene basis preferably is at least at 90% of

21 the thermal equilibrium content (or concentration). More preferably, in the present

22 invention, the xylenes in the feed are converted such that in the effluent from the

23 isomerization reaction zone, the paraxylene content on a xylene basis is at least at

24 95% of the thermal equilibrium content (or concentration). Still more preferably, in

25 the present invention, the xylenes in the feed are converted such that in the effluent

1   from the isomerization reaction zone, the paraxylene content on a xylene basis is at

2   least at 100% of the thermal equilibrium content (or concentration).

3   Within the parameters of the present invention with a trickle flow of hydrogen at low

4   pressure, an EB conversion fouling rate of the catalyst is achieved that is preferably

5   less than 1 degree F per day, and more preferably less than 0.5 degrees F per day.

6   In addition, we have found that the preferred catalyst and process conditions described

7   herein for the present invention achieve high catalyst stability from an EB conversion

8   standpoint relative to prior low pressure processes. The catalyst of the invention

9   allows operation at high/higher EB conversions than possible with prior art low

10   pressure processes, while still achieving better catalyst stability than prior art low

11   pressure processes. Note that by higher catalyst stability we mean lower catalyst aging

12   rate resulting in a longer catalyst life. The preferred catalyst and process conditions of

13   the invention also result in good initial xylene isomerization activity as demonstrated

14   by a PXATE of 100+%. In addition, while the catalyst shows excellent stability from

15   an EB conversion standpoint, the catalyst also shows excellent stability from a xylene

16   isomerization standpoint. This xylene isomerization stability is demonstrated by a

17   very slow decline in the PXATE with time. A slow decline in PXATE as described

18   herein is advantageous because it allows the cycle time between catalyst regenerations

19   to be increased and effectively decreases the overall aging rate of the catalyst.

20   As stated above, the present invention uses a catalyst comprising ZSM-5

21   aluminosilicate. Preferably, the ZSM-5 is in the hydrogen form. ZSM-5 can have

22   most of the original cations associated therewith replaced by a wide variety of other

23   cations according to techniques well known in the art. In a preferred embodiment of

24   the present invention, most of the original cations are replaced by hydrogen by

25   methods such as ammonium-exchange followed by calcination.

1　The crystal size of the ZSM-5 component of the catalyst used in the process of the
2　present invention is less than 1.0 micron, preferably less than 0.9 microns, more
3　preferably 0.2 to 0.9 microns, still more preferably 0.2 to 0.8 microns.

4　The silica/alumina ratio of the ZSM-5 of the catalyst used in the present invention is
5　in the range of 10 to 300, preferably 30 to 200, more preferably from 30 to 150, still
6　more preferably in the range of from 50 to 100, and most preferably is in the range of
7　70 to 90.

8　The preferred Group VIII hydrogenation metal for the catalyst used in the present
9　invention is platinum (Pt). Preferably, the Pt content is from 0.05 to 1.0 wt. %, more
10　preferably from 0.05 to 0.75, and still more preferably from 0.075 to 0.5 wt. %. Pt is
11　believed to act as a hydrogenation/dehydrogenation component. Although not as
12　preferred in the present invention, other Group VIII metals can be used such as
13　palladium (Pd) or nickel (Ni). The Pt may be added by ion-exchange or by
14　impregnation.

15　Palladium may be used as the Group VIII hydrogenation metal for the catalyst used in
16　the present invention. Preferably, the Pd content is from 0.1 to 2.0 wt. %, more
17　preferably from 0.1 to 1.5, and still more preferably from 0.15 to 1.0 wt. %.

18　Nickel also may be used as the Group VIII hydrogenation metal for the catalyst used
19　in the present invention. Preferably, the Ni content is from 0.10 to 20 wt. %, more
20　preferably from 0.1 to 10, and still more preferably from 1 to 8 wt. %.

21　Mixtures of Group VIII metals can also be used in conjunction with the ZSM-5 zeolite
22　to produce a catalyst suitable for use in the present invention. Mixtures such as Pt and
23　Ni; Pt and Pd; Pd and Ni; and Pt, Pd and Ni can be used in numerous different
24　proportions in the present invention to achieve a suitable catalyst.

1   The catalyst preferably comprises zeolite bound with an inorganic matrix, such as

2   alumina. A preferred form of the catalyst is bound zeolite extruded to a 1/16-in.

3   diameter extrudate.

4   The feedstock for the process of the present invention is preferably obtained from a

5   paraxylene separation process such as an adsorption process, a crystallization process,

6   or a combination of both processes.

7   Such processes remove paraxylene from a C_8 boiling range feedstocks, leaving a

8   paraxylene depleted stream. The paraxylene depleted stream contains a below

9   equilibrium level of paraxylene, preferably 0-20% by weight paraxylene, more

10   preferably 0-12% by weight paraxylene. Feeds that are obtained predominantly from

11   an adsorption process will typically have lower amounts of paraxylene in the feed

12   than a feed that is obtained from a paraxylene separation process based on

13   crystallization.

14   According to a preferred embodiment, the process of the present invention comprises

15   contacting the catalyst described herein with a C_8 aromatics stream which has a

16   paraxylene concentration which is below equilibrium on a xylenes basis and which

17   has an ethylbenzene concentration of 2-20 wt. %, preferably 5-20 wt. %, and a

18   non-aromatic concentration of between 0 and 8 wt. %, preferably 0-5 wt. %.

19   In the process of the present invention, preferably, the hydrogen is added at a rate so

20   that the mole ratio of hydrogen to ethylbenzene in the feed is preferably 1.0 to 7.0,

21   and most preferably 1.0 to 3.0. The mole ratio of hydrogen to hydrocarbon in the feed

22   is 0.02 to 1.0, preferably 0.04 to 1.0, more preferably 0.06 to 0.8, still more preferably

23   0.07 to 0.5, and most preferably 0.07 to 0.2.

1   In a preferred embodiment of the present invention, since the rate of hydrogen

2   addition is so small—a trickle—relative to the feed, there is no need to recycle the

3   unused hydrogen, thus the hydrogen is added on a once-through basis.

4   The temperature used in the reaction zone is preferably 500 to 1000°F, more

5   preferably between 600 to 900°F.

6   Preferably, the reaction zone of the present invention is operated to achieve an

7   ethylbenzene conversion of at least 20 wt. %, more preferably at least 35 wt. %, still

8   more preferably at least 50 wt %, and most preferably 50 to 80 wt. %. The

9   ethylbenzene conversion/xylene loss ratio of the present process is greater than 15/1,

10   preferably greater than 20/1, and more preferably greater than 25/1.

11   Terms used in the art such as "lean in paraxylene" or "depleted in paraxylene" are

12   generally used to indicate that a given stream contains less than an equilibrium

13   amount of paraxylene relative to the other xylenes (metaxylene and orthoxylene). A

14   stream that is lean in paraxylene or depleted in paraxylene is typical of a stream that

15   has been subjected to a paraxylene separation process such as an adsorption or

16   crystallization process in order to remove the paraxylene contained therein. Such a

17   stream depleted in paraxylene is a typical feedstock to an isomerization type process

18   of the present invention.

19   An important feature of the present invention is effective removal of a portion of the

20   ethylbenzene from the C_8 feed by hydrodealkylation in the reaction zone. We have

21   found that, in the process of the present invention, the hydrodealkylation can be

22   accomplished with a surprisingly small amount of hydrogen at a surprisingly low

23   pressure. As such, we have found that a useful measure for the present invention is

24   hydrogen to ethylbenzene feed mole ratio, since the primary purpose of the hydrogen

25   is to participate in the hydrodealkylation of the ethylbenzene. Stoichiometrically, one

26   mole of hydrogen is required to hydrodealkylate one mole of ethylbenzene. Thus, the

1   theoretical minimum amount of hydrogen required to hydrodealkylate 50% of the

2   ethylbenzene in the feed is a hydrogen to ethylbenzene mole ratio of 0.5. In practice,

3   more hydrogen is required since all of the hydrogen does not react and some of the

4   hydrogen reacts with molecules other than ethylbenzene. For example, the hydrogen

5   may be used in hydrogenating cracked paraffins in the reaction zone. Hydrogen may

6   also saturate some of the aromatic rings.

7   The fouling rate of the catalyst used in the reaction zone is low under the process

8   conditions of the present invention. Fouling of an isomerization catalyst is to a great

9   extent caused by coke formation on the catalyst surface. Fouling of the catalyst

10   decreases the performance of the catalyst. The decrease in performance, that is i.e. the

11   loss in EB conversion, can be compensated for to a great extent by increasing the

12   process temperature. The process temperature can only be increased so far, however.

13   It is then necessary to regenerate the catalyst by removing the coke. If the time

14   between required catalyst regenerations is too short for a given catalyst, due to a rapid

15   fouling rate, the catalyst is not practical for a commercial unit. The rate of fouling of

16   the catalyst is thus an important factor in the desirability of the catalyst.

17   The process of the invention may be carried out in a moving bed or fixed bed reactor.

18   In a moving bed reactor and after reaching the end of a reaction cycle, the catalyst can

19   be regenerated in a regeneration section/zone where the coke is burned off from the

20   catalyst in an oxygen containing atmosphere such as air at a high temperature, after

21   which the catalyst is recycled to the reaction zone for further contact with the feed. In

22   a fixed bed reactor, regeneration can be carried out in a conventional manner by using

23   initially an inert gas which contains a small amount of oxygen, e.g., 0.5 to 2.0%, to

24   burn the coke off the catalyst in a controlled manner so as not to exceed a maximum

25   temperature of 900°F to 950°F.

1   The ZSM-5 zeolite component of the catalyst used in the process of the present

2   invention can be prepared in various manners. Suitable preparation procedures are

3   described in U.S. Pat. No. 3,702,886 to Argauer et al.

4   ZSM-5 embraces a family of crystalline aluminosilicates as set forth in more detail in

5   U.S. Pat. No. 3,702,886, the disclosure of which patent is incorporated by reference

6   into this specification.

7   The structure of the ZSM-5 class of zeolites is such that the pore sizes or apertures of

8   the zeolite are in the intermediate size range of approximately 5 to 7 Angstroms,

9   usually about 5.5 Angstroms. This is in contrast to the larger pore size zeolites, such

10   as faujasite, or the smaller pore size zeolites such Linde Type A and erionite. The

11   structure of ZSM-5 is described by Kokotailo et al. in *Nature,* Vol. 272, March 30,

12   1978, page 437. The pore opening into the crystalline zeolite is delineated by the

13   atomic structure. However, the pore opening or constraints may be modified by

14   components added to the ZSM-5.

15   Although ZSM-5 is the preferred zeolite for use in the catalyst used in the process of

16   the present invention, other zeolites of the ZSM-5 type are embraced within a broad

17   embodiment of the present invention. These zeolites include ZSM-11, which is

18   described in U.S. Pat. Nos. 3,709,979 and 4,108,881 (alternate synthesis), the

19   disclosures of which are incorporated by reference into the present specification.

20   Another publication that provides a synthesis of ZSM-11 is PCT publication

21   WO9509812-A1 (also EP 721,427-A1).

22   According to an alternate embodiment of the present invention, besides ZSM-5, other

23   intermediate pore zeolites having a pore size of approximately 5 to 7 Angstroms may

24   also be used to form the catalyst used in the process of the present invention. ZSM-11

25   is included in such other intermediate pore size zeolites. However, the most preferred

26   embodiment of the present invention uses ZSM-5 zeolite. ZSM-5 can be made in a

1   variety of ways e.g. with and without seeding, with and without templates. One way

2   of making ZSM-5 is exemplified below.

3   The ZSM-5 zeolite can be made by preparing a solution containing water, tetrapropyl

4   ammonium hydroxide and the elements of sodium oxide, an oxide of aluminum or

5   gallium, an oxide of silica, and having a composition, in terms of mole ratios of

6   oxides, falling within the following ranges:

7   TABLE I

	Broad	Preferred	Particularly Preferred
OH-/SiO$_2$	0.07-1.0	0.1-0.8	0.2-0.75
R$_4$N+/(R$_4$N+ + Na+)	0.2-0.95	0.3-0.9	0.4-0.9
H$_2$O /OH-	10-300	10-300	10-300
SiO$_2$/Al$_2$O$_3$	5-120	20-110	70-100

8

9   wherein R is propyl. This mixture is maintained at reaction conditions until the

10   crystals of the zeolite are formed. Thereafter, the crystals are separated from the

11   liquid and recovered. Typical reaction conditions consist of a temperature of from

12   about 160°F to 400°F for a period of about 2 days to 60 days. A more preferred

13   temperature range is from about 190°F to 235°F, with the amount of time at a

14   temperature in such range being from about 7 days to 21 days.

15   The digestion of the gel particles is carried out until crystals form. The solid product

16   is separated from the reaction medium, as by cooling the whole to room temperature,

17   filtering and water washing.

18   ZSM-5 is preferably formed as an aluminosilicate. The composition can be prepared

19   utilizing materials which supply the elements of the appropriate oxide. Such

1   compositions include aluminosilicate, sodium aluminate, alumina, sodium silicate,

2   silica hydrosil, silica gel, silicic acid, sodium hydroxide and tetrapropylammonium

3   hydroxide. Each oxide component utilized in the reaction mixture for preparing a

4   member of the ZSM-5 family can be supplied by one or more initial reactants. For

5   example, sodium oxide can be supplied by an aqueous solution of sodium hydroxide,

6   or by an aqueous solution of sodium silicate. The reaction mixture can be prepared

7   either batchwise or continuously. Crystal size and crystallization time of the ZSM-5

8   composition will vary with the nature of the reaction mixture employed. The zeolite

9   contains tetrapropylammonium cations which are removed by calcination producing

10   the H-Na form of the zeolite.

11   The zeolites used in the instant invention may have a certain proportion of the original

12   cations associated therewith replaced by other cations. Exchange techniques known

13   in the art may be used. Preferred replacing cations include ammonium and metal

14   cations, including mixtures of the same. Preferably, the replacing cation is

15   ammonium, and preferably the ammonium is converted to hydrogen by driving off

16   ammonia to result in the replacing cation being hydrogen. Thus, as stated above

17   preferably the ZSM-5 used to form the catalyst used in the present invention is

18   predominantly in the hydrogen form.

19   By predominantly in the hydrogen form, we mean that a dominant characteristic of the

20   ZSM-5 used to form the catalyst is that the ZSM-5 is in an acidic form as opposed to a

21   basic form. A basic form is one where the ZSM-5 has substantial amounts of the

22   original sodium; that is, the sodium that is present in the as-synthesized ZSM-5.

23   Accordingly, preferably at least 80% of the sodium ions in the ZSM-5 used to form

24   the catalyst have been replaced by hydrogen ions, more preferably at least 90%, still

25   more preferably at least 95%, and most preferably at least 98% of the sodium ions

26   have been replaced by hydrogen ions.

1   In accordance with these percentage removals, the amount of sodium left in the

2   ZSM-5 will depend on the original amount present, which in turn will depend on

3   factors such as the silica to alumina ratio. Keeping these qualifications in mind,

4   ranges for sodium left in the ZSM-5 after it has been converted to the hydrogen form

5   preferably are less than 0.1 wt. % of the original sodium, more preferably less than

6   0.06 wt. %, and most preferably less than 0.03 wt. %.

7   Typical ion exchange techniques include contacting the zeolite with a salt of a

8   replacing cation or cations. Although a wide variety of salts can be employed,

9   particular preference is given to chlorides, nitrates and sulfates.

10   In the process of the present invention, it is preferred to use the zeolite in a "bound"

11   form, that is, with a refractory oxide as a binder for the overall catalyst particle.

12   Suitable refractory oxide binders are alumina, silica, titania, clay, or mixtures thereof.

13   This binder serves to hold the crystalline zeolite particles together in a catalyst particle

14   of suitable size and suitable attrition resistance upon handling and use in the

15   isomerization process. The amount of binder used versus zeolite is preferably

16   between 10 and 65 percent binder by weight, more preferably between 20 and

17   50 percent binder.

18   Alumina is a particularly effective binder for the catalyst used in the ethylbenzene

19   hydrodealkylation/isomerization process of the present invention. A preferred form of

20   the alumina is that commonly referred to as Catapal-B, available from Condea-Vista

21   Company.

22   A typical catalyst is in the form of a 1/16-inch diameter by 3/16-inch length extrudate.

23   Use of the zeolite powdered catalyst as prepared would result in too high a pressure

24   drop in the preferred fixed bed used in the ethylbenzene

25   hydrodealkylation/isomerization process.

1   The added hydrogenation metal, such as the preferred platinum, palladium, or nickel

2   used in the catalyst, may be added to the catalyst by impregnation or ion exchange

3   using known techniques. In general, the metals are added as salts, preferably of

4   thermally decomposable anions such as the nitrate, nitrite, acetate, etc., or soluble

5   metal complexes, by filling the pores of the catalyst with a solution of appropriate

6   concentration to achieve the desired metal loading, equilibrating, drying and calcining

7   to remove solvent, impurities and to decompose the salts to remove the volatile

8   products. Alternatively, adsorption or other techniques well known in the art for

9   introducing metals into porous substances may also be used.

10   BRIEF DESCRIPTION OF THE DRAWINGS

11   FIG. 1 is a schematic flow diagram illustrating the positioning of the ethylbenzene

12   hydrodealkylation/isomerization reaction zone in a process sequence directed to

13   producing paraxylene.

14   FIG. 2 is a graph illustrating the stability of PXATE for various ZSM-5 catalysts.

15   DETAILED DESCRIPTION OF THE DRAWINGS

16   Referring now in more detail to FIG. 1, a mixed aromatic/paraffin feed in line 1 is

17   combined with the line 2 effluent stream from ethylbenzene

18   hydrodealkylation/isomerization zone 15. The combined streams are fed via line 3 to

19   column 4 for distillation. The higher boiling aromatics—those having more than

20   8 carbon atoms—are taken as a bottoms fraction in line 5; the overhead comprising C_8

21   aromatics and lighter components is charged via a line 6 to another distillation unit

22   column 7. In this second distillation column, the lower boiling aromatics—those

23   having less than 8 carbon atoms—and any paraffinic components, are taken overhead

24   in line 8. The bottoms from the second distillation, comprising C_8 aromatics, are then

25   fed via line 9 to paraxylene separation zone 10.

1   In separation zone 10, about 25 to 95 percent of the paraxylene is removed by

2   crystallization or by extraction. The crystallization can be carried out by low

3   temperature processes, and extraction can be carried out by various processes, for

4   example, the UOP "Parex Process" or the IFP "Eluxyl Process". Separated

5   paraxylene is withdrawn via line 11 from zone 10.

6   The effluent (mother liquor) from the separation zone 10 is withdrawn via line 12 and

7   is fed to ethylbenzene hydrodealkylation/xylene isomerization zone 15 which uses

8   reaction conditions according to the present invention, as described above.

9   Provision is made via line 13 to bleed some of the paraxylene plant mother liquor as

10 desired.

11 Gaseous hydrogen is fed into the ethylbenzene hydrodealkylation/xylene

12 isomerization zone 15 via line 16. In accordance with a preferred embodiment of the

13 present invention, only once-through hydrogen is used. Light gasses are removed

14 from the ethylbenzene hydrodealkylation/isomerization zone 15 via line 17.

15 Finally, the ethylbenzene depleted, xylene isomerized stream from the ethylbenzene

16 hydrodealkylation/xylene isomerization zone 15 is withdrawn via line 2 and is

17 recycled to be combined with the incoming fresh feed.

18 Fresh feed to the process of the present invention preferably contains about 2 to

19 20 weight percent, preferably 5 to 20 weight percent, ethylbenzene based on C_8

20 aromatics. When operating this process in a continuous manner, the quantity of

21 recycled C_8 aromatics is from 2 to 4 times that of the fresh feed; and the ethylbenzene

22 in the feed to the paraxylene plant levels out at about 5 to 25 percent.

23 Figure 2 is a graph of stability of PXATE for the ZSM-5 catalysts as discussed in the

24 examples. The graph illustrates that the Pt ZSM-5 catalyst and process of the present

1   invention maintains a stable PXATE while the comparative catalysts that contain

2   magnesium show a declining PXATE.

3   Measurement of ZSM-5 Crystal Size by SEM

4   The method used is based on scanning electron microscopy (SEM). SEM is a

5   common analytical technique for examining the morphology of materials at high

6   magnifications. The range of magnifications for a common SEM instrument is

7   typically 20x to 50,000x.

8   I.   Specimen Preparation

9   For the purpose of this specification, the SEM sample was prepared by

10   mounting a small amount of the zeolite powder onto an SEM specimen stub.

11   The description of the procedure can be found in many standard microscopy text

12   books. The procedure used to determine all of the crystal sizes given herein was

13   as follows:

14   Step 1.   A double sided sticky carbon tape, available from microscopy supplies

15   vendors, was affixed to the specimen stub.

16   Step 2.   A small amount of zeolite powder was spread onto the carbon tape

17   using a stainless steel spatula.

18   Step 3.   The excess zeolite powder was gently blown off using an air hose or a

19   compressed air duster.

20   Step 4.   A Pd-Au alloy film (approximately 15 nm thick) was sputtered onto

21   the sample to prevent the sample from charging under the electron

22   beam.

1　　Note that (a) a representative portion of the powder was selected from the

2　　sample container, and (b) the mounting procedure was such that individual

3　　particles would be reasonably evenly spread out across the field of view at

4　　10,000x magnification.

5　II.　SEM Imaging

6　　Step 1.　The sample was surveyed at low magnifications, e.g., 500x-1000x, to

7　　　　　look for representative areas to photograph.

8　　Step 2.　At least four representative images were recorded at the 10,000x

9　　　　　magnification.

10　　Step 3.　The number of images recorded contained at least 200 zeolite crystals

11　　　　　in total.

12　III.　Image analysis to obtain number average crystal size

13　　The analysis was performed on the SEM images of 10,000x magnification. The

14　　raw data was stored in a computer spreadsheet program, e.g., Microsoft Excel,

15　　Lotus 123, etc. The objective was to obtain the arithmetic mean crystal size

16　　(d_{av}) and its standard deviation (σ), where,

17　　The arithmetic mean $d_{av} = (\sum n_i d_i)/ (\sum n_i)$

18　　The standard deviation $\sigma = (\sum (d_i - d_{av})^2/ (\sum n_i))^{1/2}$

19　　Step 1.　The recorded SEM image at 10,000x was scanned using a horizontal

20　　　　　straight edge.

1   Step 2. The longest dimension of the individual crystals parallel to the

2   horizontal line of the straight edge was measured and recorded. Those

3   particles that were clearly large polycrystalline aggregates were not

4   included in the measurement.

5   Step 3. 200 crystals were measured.

6   Step 4. The arithmetic mean (d_{av}) and the standard deviation (σ) were reported.

7   The results were cross-checked by transmission electron microscopy (TEM) to

8   assure that the crystals measured in the SEM images were actually single

9   crystals rather than polycrystalline aggregates.

10   When referring to crystal size for the ZSM-5 component of the catalyst of the

11   present invention, we mean crystal size as determined in accordance with this

12   procedure.

13   When an extrudate sample was examined and the starting zeolite powder was

14   not available, the method was altered slightly. The well sampled extrudate was

15   ground up in a mortar and pestel (not so severely as to cause loss of crystallinity

16   of the zeolite phase) and the SEM analysis was performed on the resulting

17   powder. Only those particles of the ground powder were included in the

18   analysis which could be judged to be zeolitic material from the microscopist's

19   observations of the crystalline habit (straight edges, non agglomerated binder

20   and zeolite particles, etc.). This was still cross checked by TEM where in this

21   case the sample was prepared by microtoming (or thin sectioning) and again

22   where only those particles that could be judged clearly to be zeolitic particles

23   were included in the measurement of the averages. Good agreement was

24   observed between the two methods.

1   EXAMPLES

2   The hydrocarbon feeds used in all of the process examples below were feeds obtained

3   from a commercial low pressure isomerization process. The composition of the feeds

4   is given in the table below and was determined by gas chromatographic analysis.

5   Table II
6   Feed Composition
7

	Feed I	Feed II
Component, wt %		
Non-aromatics-1	3.45	1.79
Benzene	--	--
Nonaromatics-2	1.70	0.89
Toluene	1.05	0.76
EB	6.28	7.18
PX	9.69	10.83
MX	52.28	52.42
OX	24.20	23.92
C9+ Aromatics	1.35	2.21
Total	100.00	100.00
Normalized Xylene Distribution - wt %		
PX	11.25	12.42
MX	60.67	60.14
OX	20.08	27.44
Average Molecular Weight	106.9	106.8
Specific Gravity	0.8669	0.8696

8

9   Examples 1, 2, 3 and 4 that follow describe preparation of catalysts, including

10   preferred catalysts for use in the process of the present invention. All of these

11   catalysts were made using a ZSM-5 zeolite, particularly an HZSM-5. The "H"

12   connotes that the ZSM-5 is in predominantly the hydrogen form. The HZSM-5 we

13   used was purchased from manufacturers of this zeolitic material. The following table

14   lists the HZSM-5 manufacturers and gives the crystal size of the ZSM-5.

1   The crystal size measurements were made using a Scanning Electron Microscope

2   (SEM). The number averaging method described in the section above entitled

3   *Measurement of ZSM-5 Crystal Size by SEM* was used to determine the average

4   crystal size of the ZSM-5 crystals that were used to make the catalysts.

BRIEF DESCRIPTION OF ZEOLITE SAMPLES						
Supplier	ID #	Form	Cation	Binder Amount	Crystal Size	Silica to Alumina Ratio
PQ	CBV 8020	Powder	H	None	0.7 micron	80
PQ	CBV 8062	Extrudate	H	20%	0.54 micron	80

5

6   Example 1

7   Preparation of Mg-Pt/ZSM-5 Catalyst

8   A catalyst designed to contain 1.9% Mg and 0.08% Pt on CBV 8062 was prepared

9   according to the following procedure. 325.4 grams of CBV 8062 (300 grams of

10   volatile-free extrudates) was weighed out. 62.6 grams of magnesium nitrate

11   hexahydrate, Baker (assay 99.1%), was dissolved in deionized water. The magnesium

12   nitrate solution was diluted to a volume of 115 milliliters which was calculated to be

13   100% of the total pore volume. The bound H-ZSM-5 was impregnated with the

14   solution of magnesium nitrate by the method of incipient wetness. The solution was

15   added by spraying during a fifteen-minute mixing period. The impregnated sample

16   was allowed to soak for one hour, then dried for one hour at 127°C, and calcined in a

17   preheated furnace at 500°C for one hour in flowing air. The resulting sample was

18   sized to an L/D=2 prior to the next impregnation step.

19   143 grams (140 grams volatile-free) Mg / CBV 8062 from the preceding impregnation

20   was weighed out into a round bottomed flask. 0.7318 grams of platinum tetraammine

21   dichloride from Johnson Matthey (assay 54.2% Pt) was dissolved with deionized

1 water to a total volume of 57.3 milliliters, which was calculated to be about 102% of

2 the total pore volume. The solution was used to impregnate the extrudates using the

3 method of vacuum pore filling. During the solution addition, the mass was well

4 shaken. Following the vacuum pore fill step, the mixture was allowed to soak for six

5 hours and stirred each one-half hour for the first three hours of the soak. The moist

6 catalyst was transferred to an evaporating dish. There was no excess liquid. It was

7 dried for one hour at 127 °C. It was then placed into a preheated furnace and calcined

8 in flowing air for one hour at 288 °C.

9 A microprobe analysis of the catalyst showed a non-uniform platinum distribution.

10 All of the detectable platinum was found in a shell with a steep concentration slope

11 beginning at the outer edge of the extrudate. No platinum was detected beyond about

12 20% of the distance from the edge to the center of the cross-sectioned cylinder.

13   Example 2

14   Preparation of Mg-Pt/ZSM-5 Catalyst

15 A catalyst designed to contain 1.5% Mg and 0.25% Pt on CBV 8062 was prepared

16 according to the following procedure. 371.9 grams of CBV 8062 (350 grams of

17 volatile-free extrudates) was weighed out. 57.3 grams of magnesium nitrate

18 hexahydrate, EM Science (assay 99%), was dissolved in deionized water. The

19 magnesium nitrate solution was diluted to a volume of 135 milliliters which was

20 calculated to be 100% of the total pore volume. The bound H-ZSM-5 was

21 impregnated with the solution of magnesium nitrate by the method of incipient

22 wetness. The solution was added by spraying during a fifteen-minute mixing period.

23 The impregnated sample was allowed to soak for one hour, then dried for one hour at

24 127°C, and calcined in a preheated furnace at 500°C for one hour in flowing air. The

25 resulting sample was sized to an L/D=2 prior to the next impregnation step.

1   153 grams (150 grams volatile-free) Mg / CBV 8062 from the preceding impregnation

2   was weighed out into a round bottomed flask. 6.8 grams of 70% HNO_3 was added to

3   50 milliliters of deionized water. The pH was adjusted to about 9.05 by adding 40

4   drops of concentrated ammonium hydroxide. 0.686 grams of platinum tetraammine

5   dichloride from Johnson Matthey (assay 54.7% Pt) was dissolved into the solution and

6   water was added to a total volume of 63.7 milliliters, which was calculated to be about

7   102% of the total pore volume. pH of the solution was 9.51. The solution was used to

8   impregnate the extrudates using the method of vacuum pore filling. During the

9   solution addition, the mass was well shaken. Following the vacuum pore fill step, the

10   mixture was allowed to soak for six hours and stirred each one-half hour for the first

11   three hours of the soak. The moist catalyst was transferred to an evaporating dish.

12   There was no excess liquid. It was dried for one hour at 149°C. It was then placed

13   into a preheated furnace and calcined in flowing air for 30 minutes at 288°C.

14   A microprobe analysis of the catalyst showed a uniform platinum distribution across

15   the cross-section of the extrudates.

16   Example 3

17   Preparation of Mg-Pt/ZSM-5 Catalyst

18   The procedure of Example 2 was followed to prepare a catalyst designed to contain

19   0.75% Mg and 0.25% Pt on CBV 8062. The pH of the buffered platinum

20   tetraammine dichloride impregnation solution was 9.76.

21   A microprobe analysis of the catalyst showed a uniform platinum distribution across

22   the cross-section of the extrudates.

1   Example 4

2   Preparation of Pt/ZSM-5 Catalyst Using H-ZSM-5 Extrudate

3   A catalyst designed to contain 0.25% Pt on CBV 8062 was prepared according to the

4   following procedure. 172.5 grams (160 grams volatile-free) CBV 8062 from PQ was

5   weighed out into a round bottomed flask. 7.2 grams of 70% HNO_3 was added to 50

6   milliliters of deionized water. The pH was adjusted to 9.05 by adding 40 drops of

7   concentrated ammonium hydroxide. 0.7318 grams of platinum tetraammine

8   dichloride from Johnson Matthey (assay 54.69% Pt) was dissolved into the solution

9   and water was added to a total volume of 62.4 milliliters, which was calculated to be

10   about 102% of the total pore volume. pH of the solution was 9.12. The solution was

11   used to impregnate the extrudates using the method of vacuum pore filling. During

12   the solution addition, the mass was well shaken. Following the vacuum pore fill step,

13   the mixture was allowed to soak for six hours and stirred each one-half hour for the

14   first three hours of the soak. The moist catalyst was transferred to an evaporating

15   dish. There was no excess liquid. It was dried for one hour at 149°C. It was then

16   placed into a preheated furnace and calcined in flowing air for 30 minutes at 288°C.

17   A microprobe analysis of the catalyst showed a uniform platinum distribution across

18   the cross-section of the extrudates.

19   The following table summarizes the catalysts that were prepared.

BRIEF DESCRIPTION OF CATALYST SAMPLES			
Example	% Mg	% Pt	Pt Distribution
1	1.9	0.08	Eggshell
2	1.5	0.25	Uniform
3	0.75	0.25	Uniform
4	0	0.25	Uniform

1

2 Example 5

3 Prior Art Low Pressure Xylene Isomerization Example

4 Ten grams of ZSM-5 powder CBV 8020, 0.7 micron crystal size, were formed to
5 particles of 20-40 mesh. 0.6 gm of the 20-40 mesh ZSM-5 particles were then mixed
6 with alundum and charged to a 0.5-inch diameter reactor. After dehydrating the
7 catalyst in an inert gas, namely, nitrogen, the nitrogen flow was discontinued and
8 hydrocarbon feed was passed over the catalyst.

9 For this example, Feed I was used. The feed composition is shown in Table II, above.
10 Operating conditions included a pressure of 25 psig and a WHSV of 8.8 hr^{-1}. The
11 WHSV was based on the zeolite component of the catalyst.

12 The reactor effluent was sampled periodically by an in-line sampling system and
13 analyzed by gas chromatography. The reactor temperature was adjusted to achieve a
14 nominal ethylbenzene conversion of 30 wt. %. Results are shown in Table III below.

1   Table III

Time On Stream - Hours	26.9	71.8
H_2 Added	NO	NO
H_2/EB M/M	--	--
H_2/HC Feed M/M	--	--
Pressure, Psig	25	25
WHSV, hr^{-1}	8.8	8.8
Time On-Stream - hr.	26.9	71.8
Temperature - °F	636	666
Reactor Effl.Comp. wt. %		
Non Arom.-1	8.88	4.25
Benzene	1.02	1.24
Non Arom.-2	1.11	1.34
Toluene	2.43	2.43
EB	4.39	4.32
PX	17.27	18.67
MX	42.16	44.28
OX	18.07	19.24
C_9+ Aromatics	4.68	4.26
Total	100.00	100.00
EB Conv. wt. %	30.6	31.7
Xylene loss - wt. %	10.1	4.7
EB Conv/Xyl. Loss Ratio	3.0	6.8
PX Approach To Eq. - %	88.0	92.0

Xylene Distribution - wt.%		
PX	22.29	22.71
MX	54.4	53.88
OX	23.31	23.41
PX Conc. At Eq. - wt. %	23.76	23.70
Fouling Rate - °F/hr		1.5

Two operating periods are shown, 26.9 and 71.8 hours on-stream (HOS), at a

temperature of 636°F and 666°F, respectively. Note that the ethylbenzene (EB)

conversion varied from 30.6 to 31.7 wt. %, and the xylene loss varied from 10.1 to

4.7 wt. %. This is a high xylene loss and results in an ethylbenzene conversion/xylene

loss ratio which varied from 3.0 to 6.8. In addition, the paraxylene approach to

equilibrium varied from 88-92%. In other words, the xylene isomerization was not

complete, as an equilibrium concentration of paraxylene was not reached. Indeed, at

71.8 HOS, the paraxylene concentration on a xylene basis is 22.71 versus the

equilibrium value of 23.70 wt. %. Furthermore, note that the reactor temperature had

to be increased at the rate of 1.5°F/hr in order to hold an ethylbenzene conversion of

~30 wt. %.

EXAMPLE 6

Test Of 0.08 %Pt/1.9% Mg/ZSM-5

The catalyst as prepared in Example 1 which contains 0.08% Pt and 1.9% Mg on

CBV 8062 was tested as described in Example 5 above but with some minor

1   modifications to the procedure, as described below, due to the presence of a

2   hydrogenation component and the use of hydrogen. The objective of this test was to

3   demonstrate the capability of a Pt/Mg/ZSM-5 catalyst to hydrodealkylate

4   ethylbenzene to benzene and ethane and to do so with lower xylene losses than the

5   prior art low pressure process at the same EB conversion. These goals are to be

6   achieved while operating at low total system pressure and in particular at a low

7   hydrogen partial pressure. A further objective was to determine the xylene

8   isomerization stability of this catalyst by following how the Paraxylene Approach To

9   Equilibrium (PXATE) behaved with time. The activity of a catalyst to isomerize

10   xylenes to equilibrium at any point in time is determined by the degree to which the

11   paraxylene (PX) concentration on a xylene basis approaches the equilibrium value.

12   This measure is known as the Paraxylene Approach To Equilibrium or PXATE and is

13   defined as follows:

14

15   $$\text{PXATE} = \frac{(PX_{prd} - PX_{fd}) * 100}{(PX_{eq} - PX_{fd})}$$

16

17

18   Where PX_{prd} and PX_{fd} is the concentration of PX in the product and the feed,

19   respectively, on a xylene basis. Similarly, PX_{eq} is the concentration of PX on a xylene

20   basis at equilibrium. Thus if a xylene stream containing PX is isomerized such that the

21   PX concentration in the product is the same as the PX concentration at equilibrium,

22   then the PXATE is 100%.

23

24   Since the catalyst of Example 1 is a bound extrudate, and contains 80% of the ZSM-5

25   zeolite and 20% of an alumina binder, 0.75 grams sized to a particle size of 14-28

26   mesh, was charged to the reactor. This 0.75 gram charge equates to 0.6 gm of zeolite

27   and is equivalent to the quantity of zeolite charged to the reactor in Example 5. In

28   addition, following the catalyst dehydration step as in Example 5, the catalyst of this

29   example was also treated in hydrogen at 950°F for one hour. Operating conditions in

1   the reactor included a pressure of 35 psig and a WHSV of 8.8 hr-1 based on the

2   zeolite content of the catalyst or 7.0 hr-1 based on the extrudate charged. Hydrogen

3   was added to the reactor on a once-through basis at a rate equivalent to a

4   H_2/ethylbenzene (EB) mole ratio of 1.2/1. This is equivalent to a H_2/hydrocarbon feed

5   mole ratio of 0.086. The EB conversion target was 50%. Following the treatment

6   with hydrogen, the temperature was reduced to 675°F and the feed introduced. The

7   temperature was then increased until an EB conversion of 50% was attained. It

8   should also be noted that the crystal size of the ZSM-5 zeolite contained in CBV 8062

9   is 0.54 microns. The feed used in this example was Feed II with the composition as

10   shown in Table II. The catalyst was tested for a total of 671 hours. Results are shown

11   in the Table below as a function of time on stream and in Figure 2.

12

Hours On Stream	49.5	199.1	551.6	608.0
Temperature - F	710	731	803	805
EB Conversion- wt %	49.95	50.55	53.85	52.29
Xylene Loss – wt %	3.00	2.80	2.56	2.18
EBC/XYLLR	16.67	18.07	21.06	24.03
PXATE - %	106.2	104.9	100.4	97.5

13   EBC/XYLLR = EB Conversion/Xylene Loss Ratio

14

15   The results show that a much higher EB conversion is achieved with the catalyst of

16   Example 6 than the prior art catalyst and low pressure process of Example 5. In

17   addition the xylene losses to achieve a given EB conversion are lower for the catalyst

18   of Example 6 than the prior art catalyst. For this example where the nominal EB

19   conversion was 50%, the xylene losses varied from 2.18 to 3.00% compared to 4.7 to

20   10.1% for the prior art catalyst where the nominal EB conversion was 30%. This

1   better xylene selectivity is shown by a higher EB conversion/xylene loss ratio

2   (EBC/XYLLR) which for the catalyst of this example varied from 16.67 to 24.03

3   compared to the prior art catalyst where the EBC/XYLLR varied from 3.0 to 6.8.

4   Note that the lower the ratio for a given EB conversion, the higher the xylene losses

5   and thus the lower the xylene selectivity. Furthermore, the reactor temperature was

6   increased at the rate of 0.17°F/hr to maintain 50% EB conversion. This is an order of

7   magnitude better than the prior art catalyst where the temperature was increased at the

8   rate of 1.5°F/hr to maintain 30% EB conversion. However a drawback of the catalyst

9   of Example 6, is the steady decline in the PXATE. After 608 hours on stream (HOS),

10   the PXATE, which measures xylene isomerization activity, declined from 106.2% at

11   the beginning of the run to 97.5%, indicating that at that point, an equilibrium PX

12   concentration could not be reached. This represents an average rate of decline in the

13   PXATE of 0.0157%/hr or 0.3768%/day. From a commercial standpoint this is not an

14   acceptable decay rate in the PXATE.

15

16   EXAMPLE 7

17   Test Of 0.25% Pt/1.5%Mg/ZSM-5

18   The catalyst as prepared in Example 2 was tested as described in Example 6 using

19   Feed II. This catalyst contained about 22% less magnesium than the catalyst used in

20   Example 6. In addition the platinum content was higher. This catalyst was tested for

21   a total of 695.5 hours.

22   Results are shown in the Table below and in Figure 2.

Hours On Stream	47.5	198.7	551.4	600.0	695.5
Temperature - F	702	716	767	774	789
EB Conversion-	51.29	51.4	49.76	50.91	49.53

wt %					
Xylene Loss – wt %	3.15	2.86	3.19	2.56	1.64
EBC/XYLLR	16.27	17.98	15.62	19.85	30.19
PXATE - %	104.84	103.82	100.68	98.84	96.31

1   EBC/XYLLR = EB Conversion/Xylene Loss Ratio

2

3   The results are very similar to those obtained in Example 6. The xylene losses are

4   substantially lower than the prior art catalyst and process of Example 5, varying from

5   1.64 to 3.15% at a nominal EB conversion of 50%. This results in an EBC/XYLLR

6   which varies from 15.62 to 30.19. In addition the initial temperature required to

7   achieve 50% EB conversion is slightly lower than that in Example 6, namely 702°F

8   versus 710°F. Thus the catalyst of this example has a better initial EB conversion

9   activity than the catalyst of Example 6. Furthermore, the reactor temperature was

10   increased at the rate of 0.14°F/hr to maintain 50% EB conversion. This is an order of

11   magnitude better than the prior art catalyst where the temperature was increased at the

12   rate of 1.5°F/hr to maintain 30% EB conversion. However, just as for the catalyst in

13   Example 6, the PXATE, which measures xylene isomerization activity, declines with

14   time on stream. The PXATE declined from a value of 104.84% at the beginning of

15   the run to 96.31% after 695.5 hours on stream, the end of the run. This represents an

16   average rate of decline in the PXATE of 0.0132%/hr or 0.3159%/day. While this is a

17   16% lower decay rate in the PXATE than for the catalyst of Example 6, from a

18   commercial standpoint this is not an acceptable decay rate in the PXATE.

19

1   EXAMPLE 8

2   <u>Test Of 0.25% Pt/0.75% Mg/ZSM-5</u>

3   The catalyst as prepared in Example 3 was tested as described in Example 6 using

4   Feed II. This catalyst contained about 60% less magnesium than the catalyst used in

5   Example 6 and 50% less than the catalyst used in Example 7. The platinum content

6   was the same as the catalyst used in Example 7, namely, 0.25%. This catalyst was

7   tested for a total of 756.0 hours.

8   Results are shown in the Table below and in Figure 2.

Hours On Stream	51.8	195.7	539.7	651.9	756.0
Temperature - degrees F	670	675	690	695	696
EB Conversion- wt %	52.93	50.85	51.67	52.37	50.79
Xylene Loss – wt %	3.94	1.67	2.13	3.73	2.95
EBC/XYLLR	13.43	30.49	24.26	14.03	17.2
PXATE - %	105.85	101.90	99.52	100.47	98.06

9   EBC/XYLLR = EB Conversion/Xylene Loss Ratio

10

11   The results are very similar to those obtained in Example 6. The xylene losses are

12   substantially lower than the prior art catalyst and process of Example 5, varying from

13   1.67 to 3.94% at a nominal EB conversion of 50%. This results in an EBC/XYLLR

14   which varies from 13.43 to 30.49. In addition, the initial temperature required to

15   achieve 50% EB conversion is substantially lower than that in Example 6 and 7,

16   namely 670°F versus 710°F for Example 6 and 702°F for Example 7. Thus the

17   catalyst of this example has an even better initial EB conversion activity than the

1   catalyst of Example 7. Furthermore, the reactor temperature was increased at the rate

2   of 0.03°F/hr to maintain 50% EB conversion. This is more than an order of

3   magnitude better than the prior art catalyst where the temperature was increased at the

4   rate of 1.5°F/hr to maintain 30% EB conversion. However, just as for the catalysts in

5   Example 6 and 7, the PXATE, which measures xylene isomerization activity, declines

6   with time on stream. In this example, the PXATE declined from a value of 105.85%

7   at the beginning of the run to 98.06% after 756.0 hours on stream, the end of the run.

8   This represents an average rate of decline in the PXATE of 0.0111%/hr or

9   0.2655%/day. This decay rate of 0.2655%/day represents a 30% reduction in the

10   decay rate of the PXATE relative to the catalyst of Example 6, and 16% relative to the

11   catalyst of Example 7. However, from a commercial standpoint this is still not an

12   acceptable decay rate in the PXATE.

13

14   EXAMPLE 9

15   Test Of 0.25% Pt/ZSM-5

16   The catalyst as prepared in Example 4 was tested as described in Example 6 using

17   Feed II. This catalyst contained NO magnesium but in all other respects is identical to

18   the catalysts used in Examples 7 and 8 as it uses the same base, namely, CBV 8062

19   and has the same platinum content, namely, 0.25%. This catalyst was tested for a

20   total of 812.3 hours. Results are shown in the Table below and in Figure 2.

Hours On Stream	50.3	203.1	563.2	667.1	739.2	812.3
Temperature - F	650	668	716	735	752	762
EB Conversion- wt %	48.06	47.51	47.91	50.04	48.60	45.73
Xylene Loss – wt	4.22	2.51	2.82	2.60	2.43	2.56

%						
EBC/XYLLR	11.40	18.94	17.00	19.22	20.01	17.83
PXATE - %	102.63	102.54	102.90	102.85	102.92	103.35

1   EBC/XYLLR = EB Conversion/Xylene Loss Ratio

2

3   From a xylene selectivity and EB conversion standpoint, the results are very similar to

4   those obtained in Examples 6, 7 and 8. Thus xylene losses are substantially lower

5   than the prior art catalyst and low pressure process of Example 5, varying from 2.43

6   to 4.22% at a nominal EB conversion of 50%. Furthermore, if the first xylene loss

7   data point is ascribed to high initial catalyst activity and is rejected, then the

8   subsequent xylene losses are more representative of the xylene losses for this

9   example. In that case, the xylene losses varied from 2.43 to 2.82%. On this basis, the

10   EBC/XYLLR varied from 17.83 to 20.11. This is still a substantial improvement over

11   the prior art low pressure catalyst and process of Example 5, where the EBC/XYLLR

12   varied from 3.0 to 6.8. This lower xylene loss and higher EBC/XYLLR is a

13   **surprising** result for the catalyst of this Example. Indeed, we would have expected

14   that the xylene losses with the catalyst of this Example would be similar to that of the

15   prior art catalyst since the catalyst of this Example does not contain any magnesium

16   and neither does the catalyst of the prior art low pressure process. Magnesium when

17   added, tends to reduce catalyst acidity. Thus in both instances, i.e., Examples 5 and 9,

18   we would expect the catalyst acidity to be the same, hence we would expect a similar

19   level of xylene losses. Therefore, for the catalyst of this Example, and as in

20   Example 5, we would have expected an EBC/XYLLR of 3.0 to 6.8. At 50% EB

21   conversion, this translates to a xylene loss of from 7.35 % to 16.66%. Surprisingly

22   and as noted above, the xylene losses for the catalyst of this Example varied from

23   2.43% to 2.82%. An additional improvement is that the initial temperature required to

24   achieve 50% EB conversion is substantially lower than that in Example 8, namely

25   650°F versus 670°F for Example 8. Thus the catalyst of this example has an even

26   better initial EB conversion activity than the catalyst of Example 8 and could operate

1   for a longer period of time than the catalysts of Example 6, 7 and 8. Indeed, the

2   reactor temperature was increased at the rate of 0.15°F/hr to maintain 50% EB

3   conversion. This is an order of magnitude better than the prior art catalyst where the

4   temperature was increased at the rate of 1.5°F/hr to maintain 30% EB conversion.

5   The order of magnitude lower fouling rate for the catalysts of Examples 6-9 is due to

6   the presence of Pt in the catalysts. Pt in the presence of hydrogen, and surprisingly at

7   low pressures, i.e. low hydrogen partial pressures, changes the mechanism of EB

8   conversion from disproportionation as in Example 5, the prior art low pressure

9   catalyst and process, to hydrodealkylation (to benzene and ethane) as in

10 Examples 6-9.

11 Another significant improvement with this catalyst, which does not contain any

12 magnesium, is that the PXATE does not decline with time on stream. Thus at the

13 beginning of the run the PXATE was 102.63% and at the end of the run the PXATE

14 was 103.35%, oscillating around 102.9% during the run. Thus the PXATE is very

15 stable for the catalyst of this Example.

16

17 This means that a Pt/ZSM-5 catalyst which does not contain any magnesium, would

18 maintain its full xylene isomerization activity, i.e., PXATE, for a substantially longer

19 period of time than a Pt/Mg/ZSM-5 catalyst. Furthermore, a Pt/ZSM-5 catalyst still

20 provides the benefits of a lower xylene loss-at a given EB conversion-and hence a

21 higher EBC/XYLLR than the prior art low pressure catalyst and process. Also the

22 Pt/ZSM-5 catalyst is comparable in its xylene losses and EBC/XYLLR, to the

23 magnesium containing catalysts, i.e., Pt/Mg/ZSM-5. All in all the Pt/ZSM-5 is a

24 better catalyst than the Pt/Mg/ZSM-5 and is commercially acceptable.

25

1   COMPARATIVE EXAMPLE A

2   Comparison Of Catalyst Of The Present Invention

3   To Catalyst Based On Large Crystal Size ZSM-5

4

5   The catalyst of the present invention which was prepared as in Example 4 and whose

6   performance is described in Example 9, was compared to the performance of a

7   platinum containing large crystal size ZSM-5. The performance of this platinum

8   containing large crystal size ZSM-5 is described in U. S. 4,899,011, Example 1 and is

9   identified as Catalyst A. The detailed results are shown in Table I in that reference

10   and are summarized here for simplicity. Catalyst A is a ZSM-5 zeolite with a crystal

11   size of approximately 2.5 – 4.0 microns. The catalyst contains 0.3% Pt and is a 1/16

12   inch diameter extrudate which consists of 65 wt. % zeolite and 35 wt. % alumina

13   binder. The extrudate catalyst has an alpha value of about 200 before Pt

14   impregnation. Alpha value is a measure of catalyst acidity as described in

15   U. S. 4,899,011. The high alpha value of 200 indicates that this is a highly acidic

16   catalyst with a silica/alumina ratio of about 47. Catalyst A was tested at 200 PSIG and

17   800°F. The remaining operating conditions and the results are summarized in the

18   following Table.

Time On Stream-Hours	3.5	9.5	16.0
WHSV – hrs-1	2.9	8.6	8.7
H_2/HC – Mole Ratio	2.9	3.0	3.0
EB Conversion – wt %	99.6	99.6	99.0
Xylene Loss – Wt %	13.9	4.8	13.9
EBC/XYLLR	7.17	20.75	7.12
PXATE - %	62.7	49.4	54.0

19   EBC/XYLLR = EB Conversion/Xylene Loss Ratio

20

1   The first thing to note is that this highly acidic but large crystal size ZSM-5,

2   Catalyst A, is a poor xylene isomerization catalyst on it's own and indeed has poor

3   xylene isomerization activity. This is evidenced by the extremely low value of the

4   PXATE, namely 54.0 – 62.7%. Note that it is substantially lower than the results

5   obtained with any of the catalysts discussed in this invention and in particular the

6   catalyst of this invention where the PXATE was consistently well above 100% during

7   an 812 hour test as described in Example 9. In addition, Catalyst A , has the same

8   deficiency, from the standpoint of a stable PXATE, as do the Pt/Mg/ZSM-5 catalysts

9   described in Examples 6,7 and 8. Note that for Catalyst A, the PXATE declines from

10   an initial value of 62.7% (at 3.5 hours on stream) to 54.0% after 16.0 hours on stream.

11   This represents a decline in the PXATE of 0.6960%/hr or 16.7%/day. Again, this

12   decline rate is extremely high especially when compared to the catalyst of this

13   invention, as described in Example 9, which in an extended test lasting 812 hours had

14   an initial PXATE of 102.63% and showed no significant decline in the PXATE which

15   was 103.35% at the end of the test.

16

17   Thus it is clear from this Comparative Example that for a low pressure EB

18   Hydrodealkylation and Xylene Isomerization Process with a low H_2/EB mole ratio

19   (thus very low H_2/HC feed mole ratio) and using hydrogen on a once-through basis,

20   i.e., trickle hydrogen, a large crystal size ZSM-5 catalyst, such as Catalyst A is not

21   preferred.

1   WHAT IS CLAIMED IS:

2   1.   A process for the hydrodealkylation of ethylbenzene and the isomerization of

3   xylenes, comprising contacting, in a reaction zone, a hydrocarbon feed

4   containing ethylbenzene and xylenes, with a catalyst comprising ZSM-5, and a

5   Group VIII metal comprising platinum, wherein the paraxylene content of the

6   xylenes in the feed is less than an equilibrium amount, the contacting is carried

7   out in the presence of gaseous hydrogen, and the ZSM-5 has a crystal size of

8   between 0.2 and 0.9 microns; at reaction zone conditions to hydrodealkylate

9   ethylbenzene to produce benzene and isomerize xylenes to produce paraxylene;

10   and wherein the reaction zone conditions comprise a reaction zone pressure

11   below 125 psig and a hydrogen to ethylbenzene mole ratio of 0.3 to 15.

12   2.   A process in accordance with Claim 1 wherein the ZSM-5 crystal size is

13   between 0.2 and 0.8 microns.

14   3.   A process in accordance with Claim 1 wherein the hydrogen to ethylbenzene

15   mole ratio is between 1.0 and 11.

16   4.   A process in accordance with Claim 3 wherein the ZSM-5 has a silica to

17   alumina ratio of between 10 and 300.

18   5.   A process in accordance with Claim 1 wherein reaction zone conditions

19   comprise a temperature of 500°F to 1000°F, a pressure of below 90 psig, a

20   WHSV of 2 to 20, and a hydrogen to ethylbenzene feed mole ratio of 1.0 to 7.0.

21   6.   A process in accordance with Claim 5 wherein the ZSM-5 is predominantly in

22   the hydrogen form.

23   7.   A process in accordance with Claim 1 wherein the feed comprises at least

24   70 wt. % C_8 aromatics.

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1   8.   A process in accordance with Claim 4 wherein the catalyst contains 0.05 to
2   1.0 wt. % platinum, and the ZSM-5 crystal size is between 0.2 and 0.8 microns.

3   9.   A process in accordance with Claim 1 where the reaction zone pressure is 10 to
4   80 psig, the hydrogen to ethylbenzene mole ratio is between 1.0 and 7.0, the
5   ZSM-5 crystal size is between 0.2 and 0.8 microns, the ethylbenzene content of
6   the reaction zone effluent is reduced by at least 50% compared to the
7   ethylbenzene content in the feed, and the xylenes are isomerized in the reaction
8   zone so that the paraxylene content is greater than 90% of its equilibrium value
9   on a xylene basis.

10   10.   A process in accordance with Claim 9 wherein the reaction zone effluent has an
11   ethylbenzene conversion to xylene loss ratio of greater than 15.

12   11.   A process in accordance with Claim 9 wherein the xylenes are isomerized in the
13   reaction zone so that the paraxylene content is greater than 95% of its
14   equilibrium value on a xylene basis.

15   12.   A process in accordance with Claim 9 wherein the hydrogen to ethylbenzene
16   mole ratio is between 1.0 and 3.0.

17   13.   A process in accordance with Claim 9 wherein the ZSM-5 has a silica to
18   alumina ratio is between 30 and 150.

19   14.   A process in accordance with Claim 1 wherein there is no recycle of hydrogen.

20   15.   A process in accordance with Claim 13 wherein the silica to alumina ratio is
21   between 50 and 100.

1   16.   A process in accordance with Claim 14 wherein the process for the

2   hydrodealkylation of ethylbenzene and the isomerization of xylenes is a

3   commercial process.

4   17.   A process in accordance with Claim 14 wherein the hydrocarbon feed is

5   contacted with the catalyst in the reaction zone at a rate of at least 500 bbl per
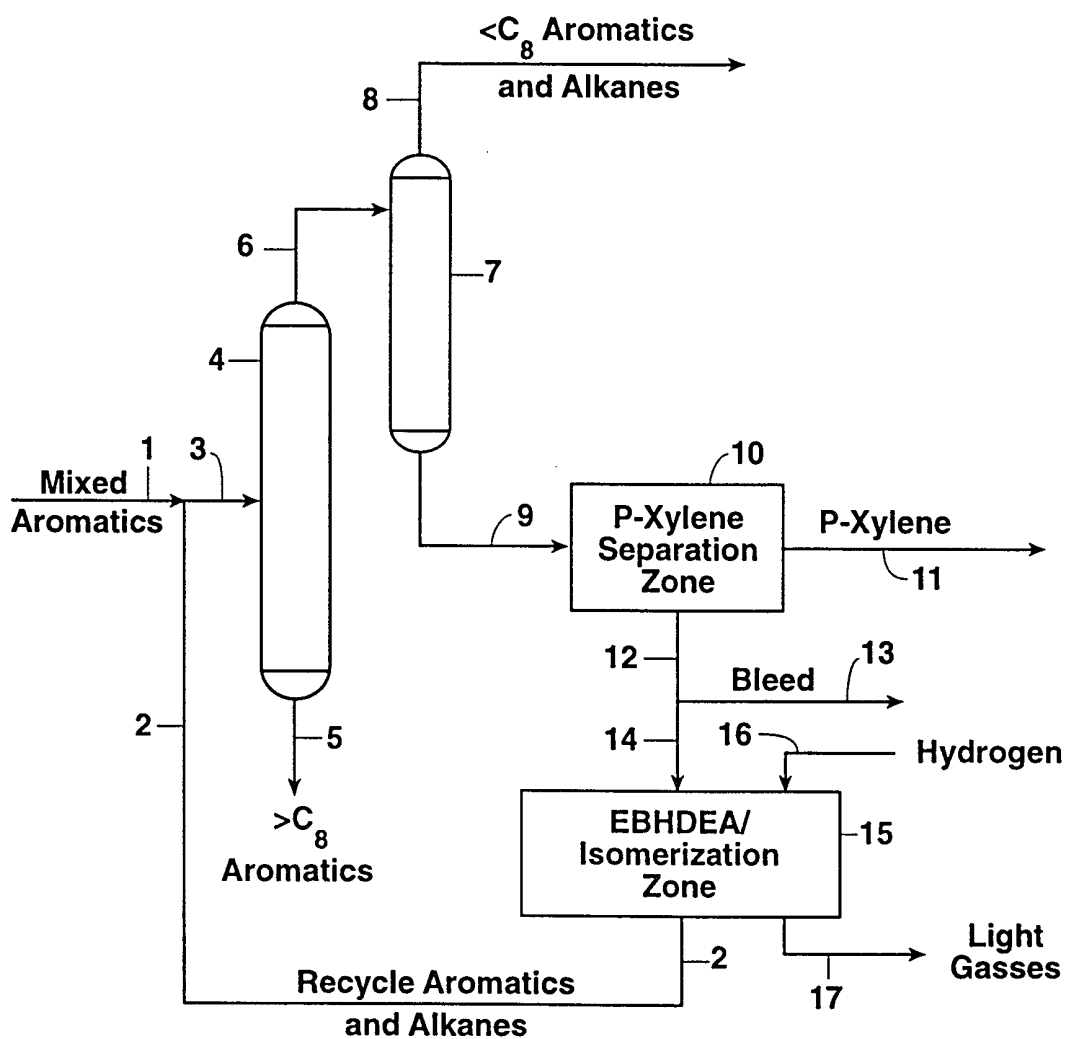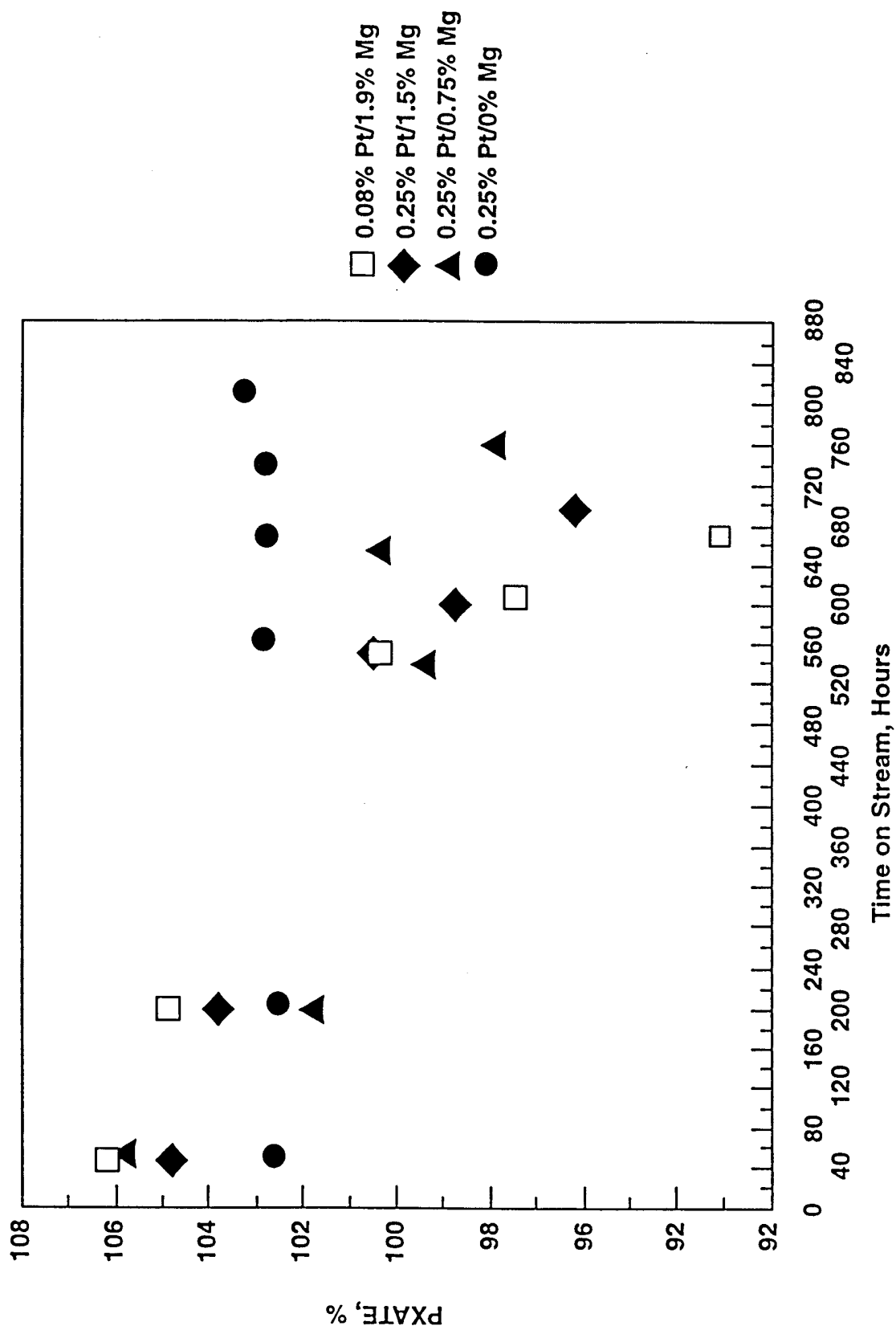
6   day.

7

1/2

Fig. 1

Fig. 2
Stability of PXATE for Various ZSM-5 Catalysts

Legend:
□ 0.08% Pt/1.9% Mg
♦ 0.25% Pt/1.5% Mg
◄ 0.25% Pt/0.75% Mg
● 0.25% Pt/0% Mg

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C07C15/08   C07C5/27   C07C4/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C07C   B01J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 43932 A (CHEVRON CHEMICAL COMPANY) 8 October 1998 (1998-10-08) claims	1-17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
23 March 2000	31/03/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

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