(51) International Patent Classification 5:
C07C 2/58, 5/52

(11) International Publication Number: WO 95/01318
(43) International Publication Date: 12 January 1995 (12.01.95)

(21) International Application Number: PCT/US94/06833
(22) International Filing Date: 16 June 1994 (16.06.94)

(30) Priority Data:
084,059 30 June 1993 (30.06.93) US

(71) Applicant: MOBIL OIL CORPORATION (US/US); 3225 Gallows Road, Fairfax, VA 22037 (US).


(74) Agents: SUNG, Tak, K. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).


Published
With international search report.

(54) Title: CATALYST WITH AN INERT BINDER FOR THE PRODUCTION OF ETHYLBENZENE

(57) Abstract
A process for producing ethylbenzene, wherein benzene is alkylated with ethylene in a vapor phase reaction over a catalyst comprising ZSM-5 and an inert, non-alumina binder, such as silica.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th>AT</th>
<th>Austria</th>
<th>GB</th>
<th>United Kingdom</th>
<th>MR</th>
<th>Mauritania</th>
</tr>
</thead>
<tbody>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GE</td>
<td>Georgia</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GN</td>
<td>Guinea</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KP</td>
<td>Democratic People’s Republic of Korea</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d’Ivoire</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LV</td>
<td>Latvia</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>MC</td>
<td>Monaco</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MG</td>
<td>Madagascar</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
This invention provides an improved process for the production of ethylbenzene using a catalyst with an inert binder.

Ethylbenzene is a valuable commodity chemical which is currently used on a large scale industrially for the production of styrene monomer. Ethylbenzene may be produced by a number of different chemical processes but one process which has achieved a significant degree of commercial success is the vapor phase alkylation of benzene with ethylene in the presence of a solid, acidic ZSM-5 zeolite catalyst. In the production of ethylbenzene by this process, ethylene is used as the alkylation agent and is reacted with benzene in the presence of the catalyst at temperatures which vary between the critical temperature of benzene up to 900°F (about 480°C) at the reactor inlet. The reactor bed temperature may be as much as 150°F (about 85°C) above the reactor inlet temperature and typical temperatures for the benzene/ethylene reaction vary from 600°F to 900°F (315°C to 480°C), but are usually maintained above about 700°F (about 370°C.) in order to keep the content of the more highly alkylated benzenes such as diethylbenzene at an acceptably low level. Pressures typically vary from atmospheric to 3000 psig (about 20785 kPa abs) with a molar ratio of benzene to ethylene from about 1:1 to 25:1, usually about 5:1 (benzene:ethylene). Space velocity in the reaction is high, usually in the range of 1 to 6, typically 2 to 5, WHSV based on the ethylene flow, with the benzene space velocity varying accordingly, in proportion to the ratio of the reactants. The products of the reaction include ethylbenzene which is obtained in increasing proportions as temperature increases together with various polyethylbenzenes, principally diethylbenzene (DIEB). Under favorable operating conditions on the industrial scale, an ethylene conversion
in excess of 99.8 weight percent may be obtained at the start of the cycle.

In the commercial operation of this process, the polyalkylated benzenes, including both polymethylated and polyethylated benzenes, are recycled to the alkylation reactor in which the reaction between the benzene and the ethylene takes place. By recycling the by-products to the alkylation reaction, increased ethylbenzene production is obtained as the polyethylated benzenes (PEB) are converted to ethylbenzene (EB). In addition, the presence of the PEB during the alkylation reaction reduces formation of these species through equilibration of the components because at a given feed composition and under specific operating conditions, the PEB recycle will reach equilibrium at a certain level. This commercial process is known as the Mobil/Badger process and is described in more detail in an article by Francis G. Dwyer, entitled "Mobil/Badger Ethylbenzene Process—Chemistry and Catalytic Implications", appearing on pages 39–50 of a book entitled *Catalysis of Organic Reactions*, edited by William R. Moser, Marcel Dekker, Inc., 1981.

Ethylbenzene production processes are described in U.S. Patents Nos. 3,751,504 (Keown), 4,547,605 (Kresge), and 4,016,218 (Haag); reference is made to these patents for a detailed description of such processes. The process described in U.S. 3,751,504 is of particular note since it includes a separate transalkylation step in the recycle loop which is effective for converting a significant proportion of the more highly alkylated products to the desired ethylbenzene product. Other processes for the production of ethylbenzene are disclosed in U.S. Patents Nos. 4,169,11 (Wight) and 4,459,426 (Inwood), in both of which a preference for large pore size zeolites such as zeolite Y is expressed, in distinction to the intermediate pore size zeolites used in the processes described in the Keown, Kresge and Haag patents. U.S. Patent No. 3,755,483
(Burress) describes a process for the production of ethylbenzene using zeolite ZSM-12 as the alkylation catalyst.

Until the late 1970's, the manufacture of alkylated aromatics such as ethylbenzene (EB) was carried out mostly by classic Friedel-Craft chemistry using aluminum chloride catalyst. The process was carried out under liquid phase conditions. Product quality was good with low impurity levels, but the process suffered from the usual disadvantages associated with aluminum chloride chemistry, namely, corrosivity of the catalyst and environmental costs associated with end-of-life disposal of spent catalyst. Since their introduction, zeolite catalysts have captured the major portion of all new capacity in aromatic alkylation processes.

Over a period of time, ranging from two weeks to more than a year, depending upon the process conditions used, alkylation catalysts gradually deactivate due to buildup of heavy aromatic hydrocarbons or coke. In the Mobil/Badger EB process, this deactivation is easily reversed by periodic in-situ regeneration of the catalyst by means of controlled air burn. Long cycle lengths between regenerations are preferred to maintain smooth operation and to reduce regeneration costs. High space velocity and, therefore, small catalyst fill are needed to allow efficient in-situ regeneration, with controllable exotherms during the coke burn.

Process economics are significantly impacted by degree of conversion of the olefin feed. Typical conversions are better than 99.5% in modern plants. In some cases, the catalyst must also be capable of high per-pass conversion of recycled polyalkylated aromatics.

In addition to causing catalyst deactivation via coking, heavy, non-recyclable materials formed must be removed from the process stream, causing a yield penalty. This is especially true of non-shape selective catalysts
such as AlCl₃, and even the large pore zeolites. With medium pore zeolite catalysts such as ZSM-5, residue rejection rates are frequently as low as 0.5%.

By-products formed during the alkylation process can cause significant problems, especially if they are co-boilers with desired products. In the EB process, for example, thermodynamics favors the conversion of ethylbenzene to xylenes. The amount of xylenes formed depends upon the process conditions and catalyst composition.

An approach to reducing the amount of xylenes in reactor effluent in EB manufacture is to reduce the operating temperature. However, simply reducing the temperature with no other changes reduces the ethylene conversion efficiency as well as the per-pass conversion of polyethylbenzene (PEB) recycle stream. The former increases feedstock costs per unit of EB made, while the latter increases the recycle loop traffic and utility costs. It has also been observed that conventional Mobil/Badger ethylbenzene (MEB) catalyst deactivates faster at lower temperatures, possibly due to polymerization of the unreacted olefin to coke precursors, or due to unfavorable sorption/desorption equilibrium of heavy hydrocarbons on catalyst.

In accordance with inventive subject matter described herein, there has been discovered a new EB catalyst composition, exemplified by silica bound ZSM-5 (80% zeolite, 20% silica binder) that allows lower temperature operation without incurring the penalties listed above.

The present invention provides a process for the production of ethylbenzene, the process comprising alkylating benzene with ethylene in the presence of a catalyst comprising ZSM-5 under vapor phase conditions, the vapor phase conditions being sufficient to produce ethylbenzene, wherein the catalyst comprises a binder which is an inert, non-alumina material.
There is also provided a process for the production of ethylbenzene with a low level of xylene impurity, the process comprising the steps of:

(a) alkylation benzene with ethylene in the presence of a catalyst comprising ZSM-5 under vapor phase conditions, the vapor phase conditions being sufficient to produce ethylbenzene and diethylbenzene, wherein the catalyst of this step (a) comprises a binder which is an inert, non-alumina material;

(b) separating the diethylbenzene from the ethylbenzene produced in step (a);

(c) transalkylation the diethylbenzene from step (b) with benzene in the presence of a catalyst comprising a zeolite under liquid phase conditions, the liquid phase conditions being sufficient to produce ethylbenzene; and

(d) combining the ethylbenzene produced in step (a) with the ethylbenzene produced in step (c), wherein the combined ethylbenzene product of step (d) contains less than 1000 ppm xylene impurity, preferably 800 ppm, most preferably 500 ppm xylene impurity.

Figure 1 shows ethylene conversion in the production of ethylbenzene as a function of days on stream for an alumina bound catalyst and a silica bound catalyst.

Figure 2 illustrates ethylene conversion in the production of ethylbenzene as a function of days on stream for an alumina bound catalyst and a silica bound catalyst.

Figure 3 summarizes xylene production during the production of ethylbenzene as a function of days on stream for an alumina bound catalyst and a silica bound catalyst.

Figure 4 shows heavies production during the production of ethylbenzene as a function of days on stream for an alumina bound catalyst and a silica bound catalyst.

The use of an inert binder in accordance with the present process provides significant advantages for the Mobil/Badger EB process including

(1) lower xylene make;
(2) lower residue make;
(3) no aging penalty at lower temperatures;
(4) no decrease in PEB recycle conversion; and
(5) better quality diethylbenzene (DEB); higher percentage of para isomer, which is easier to transalkylate.

The catalyst in the present vapor phase alkylation reaction comprises zeolite ZSM-5. ZSM-5 is described in U.S. Patent No. 3,702,886. The use of ZSM-5 as a catalyst in the vapor phase alkylation of benzene with ethylene is described in the aforementioned U.S. Patent No. 3,751,504. A particular form of ZSM-5, which may be used in the present process, is described in U.S. Patent No. 5,157,185.

The polyethylbenzene (PEB) by-product, including diethylbenzenes, may be recycled into the present vapor phase alkylation reactor, wherein PEB reacts with benzene in a transalkylation reaction to produce more of the desired ethylbenzene (EB) product. Alternatively, the polyethylbenzene (PEB) by-product may be reacted with benzene in a separate transalkylation reactor. The transalkylation reaction in this separate transalkylation reactor may take place under vapor phase or liquid phase conditions. When a separate vapor phase transalkylation reactor is used, the catalyst may comprise a zeolite, especially a medium pore size zeolite, such as ZSM-5. When a separate liquid phase transalkylation reactor is used, the catalyst may also comprise a zeolite, preferably a large pore zeolite, such as zeolite Y and, especially, zeolite beta. Zeolite beta is described in U.S. Patent No. 3,308,069. The use of zeolite beta as a catalyst in the liquid phase transalkylation of diethylbenzene with benzene is described in U.S. Patent No. 4,891,458.

The present process can be carried out at high ethylene conversion to produce an ethylbenzene product with very low content of impurities such as xylenes, cumene,
butylbenzene and heavy aromatic residues including the more highly alkylated benzenes. Especially when a separate liquid phase transalkylation reactor is used, the xylene level of the product may be less than about 1000 ppm, which is an important advantage commercially. By adjusting process parameters in a suitable manner, it is possible to obtain a xylene level of the product of less than 800 ppm, even less than 500 ppm, without taking any measures to remove xylene from the product.

The zeolite crystals can be shaped into a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product such as an extrudate having a particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then extruded.

The crystalline material is composited with another material which is resistant to the temperatures and other conditions employed in the process of this invention. Such materials include inert, non-alumina materials and may be synthetic or naturally occurring. Inert, non-alumina inorganic materials include silica, zirconia, titania, magnesia or mixtures of these and other oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the zeolite, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may improve the crush strength of the catalyst under commercial operating conditions and function as
binders or matrices for the catalyst. The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal content ranging from about 1 to about 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 2 to about 80 weight percent of the composite.

A preferred binder material for the present catalyst is silica. It is generally more difficult to prepare silica bound catalysts, particularly in the form of extrudates, than it is to prepare comparable alumina bound catalysts. Particular procedures for binding catalysts with silica, which may be applied to the preparation of the present silica bound EB catalysts, are described in U.S. Patent No. 4,582,815. Additional procedures for binding zeolites with silica are set forth in U.S. Patent Nos. 5,053,374 and 5,182,242.

The stability of the catalysts used in the present process may be increased by steaming. U.S. Patent Nos. 4,663,492; 4,594,146; 4,522,929; and 4,429,176, describe conditions for the steam stabilization of zeolite catalysts which can be utilized to steam-stabilize the catalyst. Reference is made to these patents for a detailed description of the steam stabilization technique for use with the present catalysts. The steam stabilization conditions typically include contacting the catalyst with, e.g., 5-100% steam at a temperature of at least about 300°C (e.g., 300-650°C) for at least one hour (e.g., 1-200 hours) at a pressure of 101-2,500 kPa. In a more particular embodiment, the catalyst can be made to undergo steaming with 75-100% steam at 315°-500°C and atmospheric pressure for 2-25 hours. The steaming of the catalyst can take place under conditions sufficient to initially increase the Alpha Value of the catalyst and produce a steamed catalyst having an enhanced Alpha Value. If desired, steaming can be continued to subsequently reduce the Alpha Value from
the higher Alpha Value to an Alpha Value which is substantially the same as or lower than the Alpha Value of the unsteamed catalyst.

The alkylation reaction between the benzene and the ethylene requires the alkylation catalyst to possess acidic activity and for this reason the catalyst will normally have a relatively high Alpha Value. Alpha Values of at least about 10 e.g. 40 or higher are typical, and Alpha Values above 100 have been demonstrated as useful in this process. A zeolite Alpha Value is an approximate indication of the catalytic cracking (acidic) activity of the catalyst compared to a standard catalyst and it gives a relative rate constant based on the activity of a highly active silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant = 0.016 sec⁻¹). The Alpha Test is described in U.S. Patent 3,354,078, in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980), to which reference is made for that description. The experimental conditions of the tests may include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, Vol. 61, p. 395. Excessive activity may lead to the production of undesired quantities of xylenes by secondary reactions and for this reason, Alpha Values of 10 to 100 will normally be adequate although higher Alpha Values, e.g. 100 to 500, may be employed.

The alkylation reaction is carried out at elevated temperatures in the vapor phase. Suitable conditions can be selected by reference to the phase diagram for benzene. In the vapor phase reaction, the conditions are selected to maintain the benzene in the vapor phase, for example, with a reactor inlet temperature which is above the temperature required to maintain the benzene in the vapor phase at the selected pressure, with a preferred maximum of about 900°F (about 480°C). Because the reaction is exothermic, the reactor bed temperature will be higher than the reactor
inlet temperatures, typically by as much as about 150°F (about 85°C) but generally it is preferred to control the exotherm to a maximum of about 100°F (55°C). In most cases, the reaction temperature will be from about 300°F (about 150°C) to about 850°F (about 455°C) with the yield of ethylbenzene increasing with increasing temperatures. Normally, a temperature of at least 500°F (about 260°C) will be used. Because the yield of PEB and certain other by-products usually decreases with increasing temperature, higher temperatures toward 900°F (about 480°C) would be preferred, although a disadvantage of these higher temperatures is that the yield of xylenes would be increased. The weight ratio of ethylbenzene to diethylbenzene produced in the vapor phase alkylation step (a) may be from about 2 to about 30.

Pressures during the vapor phase alkylation step typically are between atmospheric and about 3000 psig, (about 20875 kPa abs.) and generally will not exceed 1000 psig (about 7000 kPa). Relatively low pressures, for example, about 50 or 100 psig (about 445 or 790 kPa abs), sufficient to maintain the desired flow rates through the reaction bed will normally be satisfactory. The reaction is preferably carried out in the absence of hydrogen and accordingly the prevailing pressures are usually those of the reactant species. In a typical low pressure vapor phase operation, the temperature will be from 316°F to 482°F (about 600°F to 900°C) with the pressure from 450 to 3550 kPa abs (about 50 to 500 psig), usually 1480 to 3550 kPa abs (200 to 500 psig). The space velocity may be from about 0.1 to 10 WHSV, based on the ethylene feed, but is usually maintained at a relatively high value e.g. 1 to 10 WHSV, typically between 1 to 6 WHSV, based on the ethylene, for the gas phase reaction. The ratio of the benzene to the ethylene in the alkylation reactor is typically from 1:1 to 30:1 molar, normally about 5:1 to 20:1 and in most cases from about 5:1 to 10:1 molar. The percentage of
ethylene converted in the vapor phase alkylation step is at least 95%, preferably 98%. The weight ratio of ethylbenzene to diethylbenzene is from 2 to 30.

The use of temperatures significantly above about 510°C (950°F) is undesirable because at these high temperatures, a number of undesirable reactions occur. The reactants and the alkylated products undergo degradation resulting in the loss of the desired products as well as the reactants and in addition, undesirable residues may be formed from other side reactions. The ethylene which functions as the alkylating agent will tend to polymerize with itself, especially at high pressures or with other reactants to form resinous compounds within the reaction zone. These resinous compounds together with the degradation products may lead to the formation of coke-like deposits on the active surfaces of the catalyst which will rapidly inhibit the high activity necessary in the catalyst for acceptable conversion rates. The use of temperatures below about 900°F (about 480°C) will normally enable these problems to be maintained within acceptable bounds.

The alkylation process can be carried out as a batch-type, semi-continuous or continuous operation utilizing a fixed, fluidized or moving bed catalyst system. The process is, however, preferably operated in the general manner described in U.S. Patent No. 3,751,504 (Keown). Reference is made to U.S. 3,751,504 for a description of the process configuration. The use of a separate vapor phase transalkylation reactor in the recycle loop for the higher alkylated products is described in the Keown patent.

When a separate liquid phase transalkylation step is used, this step may be carried out at a temperature in the range of 121° to 316°C (about 250°F to 600°F) and a pressure in the range of 2170 to 6310 kPa abs (about 300 psig to 900 psig). A possible combination of temperature and pressure within these ranges involves the use of high temperatures, such as from 238° to 316°C (460°F to 600°F),
e.g., 260°C (about 500°F), and high pressures, such as from 4590 to 6310 kPa abs (650 to 900 psig), e.g., 4930 kPa abs (about 700 psig). The molar ratio of benzene to diethylbenzene in the liquid phase transalkylation step may be from about 1:1 to about 50:1. The liquid phase transalkylation step may be carried out at a weight hourly space velocity of about 1 to 50, based upon the weight of the total liquid feed to the reactor. Relatively high weight hourly space velocities within this range, such as from 10 to 40, e.g., about 25, may be used, especially when the above-mentioned combination of high temperatures and pressures are employed.

It will be understood that the hydrocarbon feed to the transalkylation step may comprise other hydrocarbons in addition to benzene and diethylbenzenes. These hydrocarbons include byproducts from the vapor phase alkylation step which are carried over along with diethylbenzenes when diethylbenzenes are removed from the ethylbenzene product from the vapor phase alkylation step. These other hydrocarbons may include cumene, butylbenzenes and other polyethylbenzenes, such as triethylbenzenes. To the extent that other polyethylbenzenes, such as triethylbenzenes, are included in the feed to the transalkylation step, these other polyalkylbenzenes can contribute to the yield of ethylbenzene products obtained via transalkylation reactions of the polyethylbenzenes with benzene.

**EXAMPLE 1**

A silica bound ZSM-5 catalyst was prepared in accordance with the procedure generally set forth in the aforementioned U.S. Patent No. 4,582,815. The catalyst had a zeolite content of 80 wt% and a silica content of 20 wt%. The silica bound catalyst had a crush strength of 9.8 kg/cm (55 lbs/inch). The catalyst was steamed in an atmosphere
comprising 100 % steam for four hours at 510°C (950°F). The steamed catalyst had an Alpha Value of 70.

**Comparative Example**

An alumina bound ZSM-5 catalyst was prepared with the same type of ZSM-5 used in Example 1. The catalyst had a zeolite content of 65 wt% and an alumina content of 35 wt%. The alumina bound catalyst had a crush strength of 10.3 kg/cm (58 lbs/inch). The catalyst was steamed in an atmosphere comprising 100 % steam for 3.5 hours at 538°C (1000°F). The steamed catalyst had an Alpha Value of about 50.

**EXAMPLE 2**

The catalyst from Example 1 was used as a catalyst for the alkylation of benzene with ethylene under conditions comprising an ethylene WHSV of 2 or 4, a benzene to ethylene weight ratio of 55 and a temperature of 399°C (750°F). For the purposes of comparison, the alumina bound catalyst was also tested under comparable conditions including an ethylene WHSV of 2 or 4, a benzene to ethylene weight ratio of 55 and a temperature of 399°C or 416°C (750°F or 780°F). Results are summarized in Figures 1-4.

Figure 1 shows the equivalence of an ethylene WHSV of 2 of the silica bound catalyst when operated at 399°C (750°F) to conventional (alumina bound) catalyst operated at 416°C (780°F) for both level of ethylene conversion and stability with time.

Figure 2 shows that the alumina bound catalyst is not stable with time when operated at an ethylene WHSV of 4 and 399°C (750°F), but the silica bound catalyst is.

Figure 3 shows the reduction in by-product xylene formation for the silica bound catalyst when the two catalysts are operated at an ethylene WHSV of 2 and the temperatures where both are stable as shown in Figure 1,
i.e., silica bound at 399°C (750°F) and alumina bound at 416°C (780°F).

Figure 4 demonstrates that fewer undesirable heavy components, diphenylmethane and diphenylethane, are formed over the silica bound catalyst than the alumina bound catalyst, again at an ethylene WHSV of 2 and the temperatures where each catalyst is stable.
CLAIMS:

1. A process for the production of ethylbenzene comprising alkylating benzene with ethylene in the presence of a catalyst comprising ZSM-5 under vapor phase conditions, the vapor phase conditions being sufficient to produce ethylbenzene, wherein the catalyst comprises 80 wt% of the ZSM-5 and 20 wt% of a silica binder.

2. A process according to claim 1, wherein the molar ratio of benzene to ethylene in the vapor phase alkylation is greater than or equal to 1 and wherein the percentage of ethylene converted in step (a) is at least 95%.

3. A process according to claim 2, wherein the weight ratio of ethylbenzene to diethylbenzene produced in vapor phase alkylation is from 2 to 30.

4. A process according to claim 2, wherein the vapor phase alkylation is carried out at a temperature of from 500°F to 900°F.

5. A process according to claim 2, wherein the vapor phase alkylation is carried out at a pressure from 450 to 3550 kPa abs and at a temperature of from 316°C to 482°C.

6. A process according to claim 2, wherein the molar ratio of benzene to ethylene in the vapor phase alkylation is from about 1:1 to 30:1, based on total feed to the reactor.
7. A process according to claim 5, wherein the molar ratio of benzene to ethylene in the vapor phase alkylation is from about 1:1 to 30:1, based on total feed to the reactor.

8. A process according to claim 1, wherein diethylbenzenes, which are produced in the reactor, wherein benzene is alkylated with ethylene, are recycled into the reactor and are transalkylated therein to produce ethylbenzene.

9. A process according to claim 1, wherein diethylbenzenes, which are produced in the reactor, wherein benzene is alkylated with ethylene, are introduced into a separate transalkylation reactor and are reacted therein with benzene under sufficient vapor phase or liquid phase conditions to produce ethylbenzene.

10. A process for the production of ethylbenzene with a low level of xylene impurity, the process comprising the steps of:
   (a) alkylating benzene with ethylene in the presence of a catalyst comprising ZSM-5 under vapor phase conditions, the vapor phase conditions being sufficient to produce ethylbenzene and diethylbenzene, wherein the catalyst of this step (a) comprises 20 wt% a silica and 80 wt% ZSM-5;
   (b) separating the diethylbenzene from the ethylbenzene produced in step (a);
   (c) transalkylating the diethylbenzene from step (b) with benzene in the presence of a catalyst comprising a zeolite under liquid phase conditions, the liquid phase conditions being sufficient to produce ethylbenzene; and
(d) combining the ethylbenzene produced in step (a) with the ethylbenzene produced in step (c), wherein the combined ethylbenzene product of step (d) contains less than 1000 ppm xylene impurity.

11. A process according to claim 10, wherein the zeolite in the catalyst of the liquid phase transalkylation step (c) is zeolite Y or zeolite beta.

12. A process according to claim 10, wherein the zeolite in the catalyst of the liquid phase transalkylation step (c) is zeolite beta.

13. A process according to claim 12, wherein the liquid phase transalkylation step (c) is carried out at a temperature in the range of 121°C to 316°C and a pressure in the range of about 300 psig to 900 psig.

14. A process according to claim 13, wherein the molar ratio of benzene to diethylbenzene in the liquid phase transalkylation step (c) is about 1:1 to about 50:1.

15. A process according to claim 14, wherein the liquid phase transalkylation step (c) is carried out at a weight hourly space velocity of about 1 to 50, based upon the weight of the total liquid feed to the transalkylation step (c).

16. A process according to claim 10, wherein the the combined ethylbenzene product from step (d) contains less than 800 ppm xylene impurity.
17. A process according to claim 15, wherein the liquid phase transalkylation step (c) is carried out at a temperature in the range of about 238°C to 316°C, a pressure in the range of 4590 to 6310 kPa abs and a weight hourly space velocity of about 10 to 40, based upon the weight of the total liquid feed to the transalkylation step (c).
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
<thead>
<tr>
<th>IPC(5)</th>
<th>:C07C 2/58, 5/52</th>
</tr>
</thead>
<tbody>
<tr>
<td>US CL</td>
<td>: 585/314, 316, 323, 467, 475</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>U.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>585/314, 316, 323, 467, 475</td>
</tr>
</tbody>
</table>

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

**NONE**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**APS** Search Terms: alkylation, transalkylation, disproportionation, ZSM, ethyl benzene, binder, silica

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US, A, 3,751,504 (Keown et al) 07 August 1973 col. 1, lines 41-54; col. 3, lines 17-73; col 6., lines 33-49; col. 7, lines 61-75; col 10, lines 51-53</td>
<td>1-17</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,891,458 (Innes et al) 02 January 1990 col. 2, lines 32-68; col. 4, lines 33-66; col. 5, lines 24-53; col. 11, lines 16-41</td>
<td>1-17</td>
</tr>
</tbody>
</table>

[ ] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

**Special categories of cited documents:**

- "A" = Document defining the general state of the art which is not considered to be of particular relevance
- "E" = Earlier document published on or after the international filing date
- "L" = Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" = Document referring to an oral disclosure, use, exhibition or other means
- "P" = Document published prior to the international filing date but later than the priority date claimed
- "T" = Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" = Document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" = Document of particular relevance; the claimed invention cannot be considered obvious without considering the document(s) cited or other documents
- "*" = Document member of the same patent family

**Date of the actual completion of the international search**

09 AUGUST 1994

**Date of mailing of the international search report**

30 AUG 1994

**Name and mailing address of the ISA/US**

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

**Authorized officer**

DENIS BAYD

**Facsimile No.**

NOT APPLICABLE

**Telephone No.**

(703) 305-3804