

12

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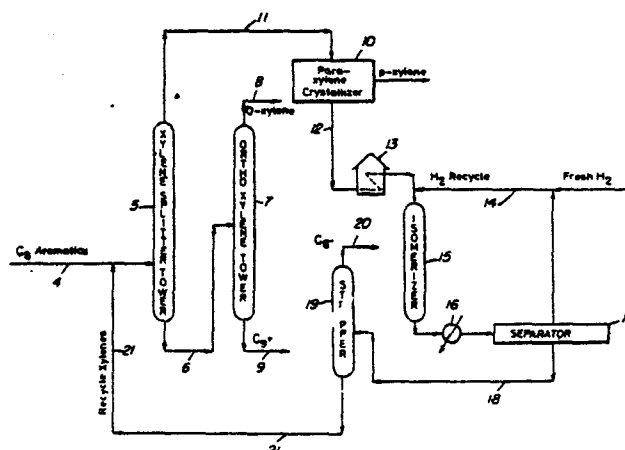
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54 A process for isomerizing xylenes.

57 Isomerization of xylenes in admixture with ethyl benzene by contact with a zeolite catalyst such as ZSM-5 is improved by use of zeolite having a silica/alumina ratio of at least 500 at a temperature above about 427°C. At these conditions, conversion of ethyl benzene follows a different reaction path which permits high conversion of ethyl benzene to benzene without loss of xylenes by disproportionation.



- 1 -

A PROCESS FOR ISOMERIZING XYLENESDESCRIPTION:

This invention relates to the isomerization of xylenes in a C₈ fraction which also contains ethylbenzene.

In a process widely practised commercially, and described inter alia in U.K. Specification 1,444,481, such xylenes are isomerized in the vapour phase employing a catalyst containing a zeolite such as ZSM-5 in the acid form. In this process the described conversion of ethylbenzene -always present in C₈ fractions- is accomplished by its disproportionation, over the catalyst, to benzene and diethylbenzene. However, since it is catalyst acidity which is responsible for this disproportionation there is a limit upon the extent to which this conversion can be permitted to proceed, since xylene losses (by their disproportionation) increase with increasing catalyst acidity.

We have now found that ethylbenzene can be converted by a reaction mechanism which is not strongly dependent on catalyst acidity, and that since the xylene isomerization reaction itself does not require a high level of catalyst acidity, given appropriate conditions,

- 2 -

that reaction can be so conducted as to avoid loss of xylenes by disproportionation whilst simultaneously converting ethylbenzene to a desirable extent.

According to the present invention a process for isomerizing xylenes mixed with ethyl benzene by contact at conversion conditions with a catalyst comprising a zeolite having a constraint index of 1 to 12, is characterized by the fact that the zeolite has a silica/alumina ratio of at least 500 and the conversion temperature is above 800°F.

The preferred zeolites are ZSM-5 itself and ZSM-5(ccM), particularly ZSM-5 (ccPt). They are advantageously employed in composited form,, the zeolite constituting from 1 to 99, preferably 5 to 80, weight percent of a composite with a binder. The temperature range usually employed is 800 to 1000°F, and the zeolite silica/alumina mole ratio can range up to 3000.

The significance and definition of "constraint index" has been widely disseminated in the patent literature, for instance in DTOS 2,438,252.

The process of the invention thus uses a zeolite of low alumina content, and therefore of low acid exchange capacity, which may also contain metals such a platinum or nickel. To compensate for the lower acid activity of the catalyst the temperature is raised to 800°F. or higher to effect xylene isomerization. At these temperatures, ethyl benzene reacts primarily via dealkylation to benzene and ethane rather than via disproportionation to benzene and diethyl benzene, a mechanism fairly independent of catalyst acidity. Since ethyl benzene conversion is less dependent on the acid function, a lower acidity catalyst can be used to

- 3 -

perform the relatively easy xylene isomerization, and the amount of xylenes disproportionated is eliminated. The reduction of xylene losses is important because about 75% of the xylene stream is recycled in the loop resulting in an ultimate xylene loss of 6-10 wt.% by previous processes.

Since most of the ethyl benzene goes to benzene instead of benzene plus diethyl benzenes, the product quality of the new process is better than that of prior practices.

The new process also allows greater flexibility with respect to charge stock. Since ethyl benzene conversion is relatively independent of isomerization, high ethyl benzene containing charge stocks can be processed, which means that charge stocks from thermal crackers (about 30 wt.% ethyl benzene) can be used as well as conventional stocks from reformers. In addition, dealkylation of C_2^+ alkyl groups is favored since the temperature is above 800°F. As a result, paraffins in the charge stock will not alkylate the aromatic rings, eliminating xylene loss via this mechanism. Thus, this new process can process paraffins in the charge by cracking them to lighter paraffins eliminating the need for their removal by techniques such as extraction. Finally, a small portion of the cracked fragments are recombined to form new aromatic rings which results in a net increase of aromatic rings.

The single figure of the drawing is a flow sheet of a typical xylene isomerization plant for processing C_8 feeds, in which the invention may be applied.

Referring to the drawing, the charge

introduced by line 4 is a mixture of eight carbon atom alkyl aromatics, namely ethyl benzene and the three xylene isomers. Such charge stocks are derived from catalytic reformates, pyrolysis gasoline, etc. by distillation and solvent extraction to separate aromatic compounds from aliphatics. The present process has the ability, unique among xylene isomerization processes, of converting paraffins, olefins and the like which are separated by the normal distillation facilities of an isomerization loop. This process is therefore capable of accepting charge materials which contain substantial quantities (say up to 15%) of aliphatic hydrocarbons. Other sources for production of xylenes include toluene disproportionation and methylation of toluene. These charge stocks contain little or no ethyl benzene and therefore cannot take advantage of the novel ethyl benzene conversion feature of the invention. However, these are acceptable charge stocks alone or in combination with fractions which contain ethyl benzene. Such charge stock passes by line 4 to a xylene splitter column 5. The bottoms from the xylene splitter, constituted by o-xylene and C₉ aromatics passes by line 6 to the o-xylene tower 7 from which o-xylene is taken overhead at line 8 and heavy ends are removed by line 9. The overhead from xylene splitter column 5 is transferred to conventional crystallization separation 10 through line 11. The crystallizer operates in the manner described in U.S. Specification 3,662,013.

Because its melting point is much higher than that of the other C₈ aromatics, p-xylene is readily separated in the crystallizer after refrigeration of the stream and a xylene mixture lean in p-xylene is transferred to an isomerization unit through line 12. The isomerization charge passes through a heater 13, is admixed with hydrogen admitted through line 14 and the

- 5 -

mixture is introduced to the reactor 15 operated in a manner presently to be described.

Isomerized product from reactor 15 is cooled in heat exchanger 16 and passes to a high pressure separator 17 from which separated hydrogen can be recycled in the process. The liquid product of the isomerization passes by line 18 to a stripper 19 from which light ends are passed overhead by line 20. The remaining liquid product constituted by C₈⁺ hydrocarbons is recycled in the system by line 21 to the inlet of xylene stripper column 5.

It will be seen that the system is adapted to produce maximum quantities of p-xylene from a mixed C₈ aromatic feed containing all of the xylene isomers plus ethyl benzene. The key to efficient operation for that purpose is in the isomerizer which takes crystallizer effluent lean in p-xylene and converts the other xylene isomers in part to p-xylene for further recovery at the crystallizer.

The reactor 15 contains a crystalline aluminosilicate (zeolite) catalyst of relatively low acid activity by reason of its very high silica/alumina ratio of 500 or higher. That catalyst, which is preferably combined with a metal from Group VIII of the Periodic Table promotes a reaction course which is unique at temperatures upwards of 800°F. Ethyl benzene in the charge is selectively cracked to benzene and ethane at little or no conversion of xylenes. The two conversions are, as noted above, decoupled such that, for the first time, reaction severity is not a compromise to achieve effective ethyl benzene conversion at "acceptable" loss of xylene. This characteristic of the process renders unnecessary the preliminary

distillation to separate at least some of the ethyl benzene from the feed stream as practiced in prior processes. It has been further found that the present process has capability to convert paraffin hydrocarbons. This makes it possible to dispense with the expensive extraction step conventionally applied to the C₈ aromatic fraction of catalytically reformed naphthas in the manufacture and recovery of xylenes. In taking advantage of this feature, the feed stream at line 4 will contain the C₈ aromatics of a reformat or the like together with the paraffins of like boiling range, mostly monanes. The paraffins in the charge are hydrocracked to lighter paraffins, including ethane, which will come off separator 17 with the recycle hydrogen in much greater quantity than that resulting from conversion of ethyl benzene. This requires modification of the usual techniques for maintaining concentration of the recycle hydrogen stream by withdrawal of a drag stream, not shown in the drawing.

The flow sheet of the drawing contemplates separate recovery of o-xylene. It will be immediately apparent that this isomer may be recycled in the system in the event o-xylene is not a desired product. In that event, splitter tower 5 is operated to take o-xylene overhead with the other C₈ aromatics and take only C₉⁺ as bottoms from tower 5.

The preferred zeolites for use according to the invention are the well known zeolites ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38, described respectively in U.S. Specifications 3,702,886, 3,709,949, 3,970,544, 4,016,245 and 4,046,859. A particularly preferred form of zeolite ZSM-5 is obtained by crystallization of the zeolite from a solution containing metal ions. Such ZSM-5 variants obtained by co-crystallization of metal

and zeolite -which we designate ZSM-5(ccM)- have proven particularly effective in the process of the invention where the variant is one -ZSM-5(ccPt)- containing 0.2 to 0.8 wt.% platinum.

The x-ray diffraction pattern of zeolite ZSM-5(ccM) manifests the following significant d-spacings:

TABLE III

<u>2θ</u>	<u>d($\text{\AA}$)</u>	<u>Relative Intensity</u>
7.90	11.2 $\pm$ 0.18	VS
8.79	10.1 $\pm$ 0.16	S
9.05	9.8 $\pm$ 0.16	VW
13.20	6.7 $\pm$ 0.11	W
13.90	6.4 $\pm$ 0.10	W
14.77	6.0 $\pm$ 0.10	W
15.00	5.92 $\pm$ 0.09	VW
15.52	5.71 $\pm$ 0.09	VW
15.87	5.58 $\pm$ 0.09	W
16.50	5.37 $\pm$ 0.09	VW
17.25	5.14 $\pm$ 0.08	VW
17.60	5.04 $\pm$ 0.08	VW
17.80	4.98 $\pm$ 0.08	VW
18.14	4.89 $\pm$ 0.08	VW
19.21	4.62 $\pm$ 0.07	VW
20.38	4.36 $\pm$ 0.07	VW
20.83	4.26 $\pm$ 0.07	VW
23.10	3.85 $\pm$ 0.06	S-VS
23.28	3.82 $\pm$ 0.06	M
23.76	3.76 $\pm$ 0.06	W-M
23.92	3.72 $\pm$ 0.06	M-S
24.29	3.66 $\pm$ 0.06	W
24.53	3.63 $\pm$ 0.06	W
24.78	3.59 $\pm$ 0.06	VW
24.54	3.49 $\pm$ 0.06	VW
25.85	3.45 $\pm$ 0.06	VW
26.18	3.40 $\pm$ 0.05	VW

- 9 -

<u>2θ</u>	<u>d($\text{\AA}$)</u>	<u>Relative Intensity</u>
26.57	3.35 ± 0.05	VW
26.97	3.31 ± 0.05	VW
27.38	3.26 ± 0.05	VW
27.58	3.23 ± 0.05	VW
28.09	3.18 ± 0.05	VW
28.38	3.14 ± 0.05	VW
29.13	3.06 ± 0.05	VW
29.40	3.04 ± 0.05	VW
29.90	2.99 ± 0.05	W
30.22	2.96 ± 0.05	VW
30.55	2.93 ± 0.05	VW
31.15	2.87 ± 0.05	VW

These values were determined by standard techniques. The radiation was the K-alpha doublet copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak height, I , and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, $100 I/I_0$, where I_0 is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in Å, corresponding to the recorded lines, were calculated. In Table III the relative intensities are given in terms of a subjective evaluation. It should be understood that this X-ray diffraction pattern is characteristic of all the species of ZSM-5 (ccM) compositions. Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silica to alumina ratio of the particular sample and the extent of thermal conditioning.

ZSM-5(ccM) can be prepared from a reaction mixture having a composition, in terms of mole ratios of oxides, falling within the following ranges:

TABLE IV

	<u>Broad</u>	<u>Preferred</u>	<u>Most Preferred</u>
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	30-3000	70-1000	70-500
Other metal, Wt. %	0.005-5	0.01-1	0.1-1.0

Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 100°C to 175°C. for a period of time of from about six hours to 120 days. A more preferred temperature range is from about 95°C. to 175°C. with the amount of time at a temperature in such range being from about 12 hours to 8 days.

The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering and water washing.

The foregoing product is dried, e.g. at 230°F., for from about 8 to 24 hours. Of course, milder conditions may be employed if desired, e.g. room temperature under vacuum.

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000°F. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F. in air. The presence of

organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about 1000°F. for from about 15 minutes to about 24 hours.

Natural zeolites may sometimes be converted to this type zeolite catalyst by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite.

In a preferred aspect of this invention, the zeolites hereof are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred zeolites of this invention are those having a constraint index as defined above of about 1 to about 12, a silica to alumina ratio of at least about 500 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g. on page 19 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference on Molecular Sieves, London, April 1967," published by the Society of Chemical Industry, London, 1968. When

the crystal structure is unknown, the crystal framework density may be determined by classical pykometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. The high density, of course, must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites are:

<u>Zeolite</u>	<u>Void Volume</u>	<u>Framework Density</u>
Ferrierite	0.28 cc/cc	1.76 g/cc
Mordenite	.28	1.7
ZSM-5, -11	.29	1.79
Dachiardite	.32	1.72
L	.32	1.61
Clinoptilolite	.34	1.71
Laumontite	.34	1.77
ZSM-4 (Omega)	.38	1.65
Heulandite	.39	1.69
P	.41	1.57
Offretite	.40	1.55
Levynite	.40	1.54
Erionite	.35	1.51
Gmelinite	.44	1.46
Chabazite	.47.	1.45
A	.5	1.3
Y	.48	1.27

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table, including, by way of example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired conversion process, it may be desirable to incorporate the above described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous

matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

In order that the invention may be more clearly understood some preferred embodiments of it are set forth by way of illustration in the following Examples.

Example 1

Zeolite ZSM-5 (ecPt) having a silica to alumina ratio of 660 and containing 0.23% by weight of platinum was prepared by heating together the following reagents:

- 16 -

Water	710 grams
Chloroplatinic acid (40 wt.% Pt.)	2
Hydrochloric acid	35
Tetraethyl Ammonium Bromide	25
Water Glass	290
8.9% Na ₂ O	
28.7% SiO ₂	
62.4% H ₂ O	
0.046% Al ₂ O ₃	

The product contained 0.23% platinum in ZSM-41 of 660 silica/alumina.

Example 2

Zeolite ZSM-5 (ccPt) having a silica to alumina ratio of 1041 and containing 0.76% by weight of platinum was prepared by heating together the following reagents:

Water	600 grams
Tetrapropylammonium bromide	100
Chloroplatinic acid (40 wt.% Pt)	3
$\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$	0.77
Tetraethyl orthosilicate	314
50% NaOH solution	21.2

After crystallization was complete, the crystals were separated by filtration, washed with water, dried, base exchanged with ammonium cation and calcined at about 1000°F.

The resultant catalyst had a silica/alumina ratio of 1041 and contained 0.76 wt.% platinum.

Example 3

A mixture of hydrocarbons was prepared which simulates charge to the isomer 15 in an operation charging at line 4 of the drawing, a fraction prepared by distillation from catalytic reformat to include the C₈ aromatics. The simulated charge contained 6.9% n-nonane, 30.7% ethyl benzene and 62.4% of a mixture of xylenes poor in p-xylene, viz. 73.3% m-xylene, 17.8% o-xylene and 8.9% p-xylene. That mixture was reacted over the catalyst of Example 1. Reaction conditions and products of the reaction are tabulated in Table V.

Example 4

The same charge as in Example 3 was processed over the catalyst of Example 2, with results as shown in Table V.

Example 5

A simulated charge was prepared by blending 9.8% ethyl benzene with 90.2% of mixed xylenes having the composition set out in Example 3. That charge approximates the isomerizer feed in a system supplied with fresh feed prepared by fractionation of catalytic reformat to separate a C₈ aromatics cut and solvent extraction to reject the paraffin content of the fraction. Results are shown in Table V on processing the simulated charge over the catalyst of Example 2.

- 19 -
TABLE V

Conversion of Simulated Charge Over ZSM-5(ccPt)
At 900°F., 200 psig, 5 Mols H₂ Per Mole of Hydrocarbon

Example No.	3	4	5
5			
Silica/alumina	660	1041	1041
Pt, % by weight	0.23	0.76	0.76
WHSV	10	4	4
Material Balance	97.31	98.74	100.27
Hours on stream	95	24	87
10			
Wt. %			
C ₂ 's PAR	5.50	5.28	1.42
C ₃ 's PAR	1.66	1.53	0.04
C ₄ 's PAR	1.35	1.29	0.01
C ₅ 's PAR	1.36	1.37	0.07
15			
C ₆ 's PAR	0.35	0.29	0.01
Benzene	13.53	13.01	2.97
C ₇ 's PAR	0.01	0.01	--
Toluene	0.90	0.81	0.57
C ₈ 's PAR	0.02	0.01	--
20			
Ethyl benzene	Charge 30.7	Charge 12.29	Charge 9.8
m-xylene	45.7	35.06	36.03
p-xylene	5.6	14.16	13.14
o-xylene	11.1	12.70	13.05
25			
C ₉ PAR	6.9	1.30	1.42
C ₉ AR	0.23	0.21	0.41
C ₁₀ ⁺ AR	0.26	0.25	0.05
Wt. % Conversion			
Ethyl Benzene	62.86	60.46	47.96
30			
Wt. % Conversion C ₉	81.59	79.42	
Mole C ₆ H ₆ / Mole Ethyl Benzene Reacted	0.95	0.96	0.96

It will be noted from the experimental data in Table V that reactions of ethyl benzene are predominantly by conversion to benzene as contrasted with disproportionation reactions which yield diethyl benzene. Although it is known that diethyl benzene can be reacted to chemical raw materials having a present market value as such, in practice the diethyl benzene is diverted to fuel use in motor gasoline and the like. The present process yields benzene as the heavily predominant product to the significant economic advantage of the overall process. It has been demonstrated that the conditions (catalyst, temperature) induce dealkylation of ethyl benzene by charging ethyl benzene alone. There are indications that dealkylation of ethyl benzene in the presence of xylene has a favorable effect on selectivity of conversion of ethyl benzene to benzene. The data are not adequate to establish a true "cause and effect" relationship but the trend of data do indicate that the ethyl benzene conversion is more selective for benzene as product when xylenes are present, despite the observed lack of the usual relationship of coupling wherein degree of xylene conversion to other compounds (xylene loss) tends in the same direction as ethyl benzene conversion.

The reaction is found to proceed in the direction indicated with metal free high silica zeolite, but is less selective than when the zeolite is associated with a metal of Group VIII. Also shorter catalyst life is to be expected with metal-free zeolite catalyst. Particularly preferred are the noble metals of Group VIII, namely platinum, palladium, osmium, iridium, ruthenium and rhodium. The other Group VIII metals, such as nickel exhibit the advantages of the invention to less extent, in some cases by minor increase of xylene loss at conditions to promote

increased ethyl benzene conversion, some apparent coupling of the reactions.

The metal should be a minor component of the catalyst, say 0.05 to 2.0 weight percent and is preferably highly dispersed. For purposes of achieving dispersion of metal, the catalyst is preferably of the ZSM-5(ccM) variety wherein the metal is present in the forming solution from which the zeolite is synthesized. When metal is applied to a fully formed zeolite, as by impregnation with conventional techniques, care must be exercised. The quantity of metal should be relatively low, say up to 0.2 weight percent. At moderate to high metal content, e.g. 0.3 to 1.0 weight percent platinum, applied by impregnation the catalyst exhibits tendency to loss of benzene rings, apparently by hydrocracking, possibly on relatively large crystals of metal within the pores of the catalyst. These problems are largely alleviated when the metal-bearing zeolite is of the ZSM-5 (ccM) variety and all the metal content is derived from metal compounds in the synthesis liquor.

Example 6

Catalyst comprising 0.18 wt.% platinum in zeolite ZSM-5(ccPt) of 2000 silica/alumina ratio was prepared from the reaction mixture:

Water	600 grams
Tetrapropyl Ammonium Bromide	100
Chloroplatinic Acid (40 wt.% Pt)	1
Tetraethyl Orthosilicate	314
$\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$	0.38
Sodium Hydroxide (50% NaOH)	21.2

Example 7

Zeolite HZSM-5 of 1000 silica/alumina ratio was prepared from the following mixture:

Water	600 grams
Tetrapropyl Ammonium Bromide	100
$\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$	0.76
Tetraethyl Ortho- silicate	314
Sodium Hydroxide (50% NaOH)	21.2

Following conversion to the hydrogen form by ammonium base exchange and calcining, portions of the zeolite were impregnated with 0.4 weight percent

platinum. A further ZSM-5 catalyst was prepared by impregnation of zeolite having 1600 silica/alumina ratio with 4.0 weight percent nickel, blending with 35 weight percent alumina and extrusion.

Examples 8 - 11

Catalyst prepared according to Example 6 and 7 were employed in processing ethyl benzene mixed with xylene in which the distribution of isomers was as described in Example 3. Conditions and results obtained are summarized in Table VI.

TABLE VI

Conversion of Ethyl Benzene/Xylene Mixtures

Example No.	8	9	10	11
Charge, Wt.% Ethyl Benzene	10	9.8	9.8	10.4
Xylene	89.5	90.2	90.2	89.5
C ₉	0.1	--	--	0.1
Catalyst Zeolite	ZSM-5(ccPt)	ZSM-5	ZSM-5	ZSM-5
Metal	0.18%Pt.	0.04%Pt	none	4.0%Ni
Temperature (°F)	900	900	900	900
Pressure (psig)	200	200	200	200
WHSV	5	10	5	10
H ₂ /HC	5	5	5	5
Material Balance	96.49	100.01	99.39	98.08
Hours on Stream	3	6	2	43
Wt.%				
C ₂ 's PAR	0.47	0.56	0.96	1.50
C ₃ 's PAR	0.03	0.02	0.03	0.01
C ₄ 's PAR	0.01		0.01	0.01
C ₅ 's PAR	0.02	0.01	0.02	0.01
C ₆ 's PAR				0.02
Benzene	3.03	2.16	2.74	4.39
Toluene	0.54	0.42	0.56	1.29
C ₉ 's PAR	0.01	0.01	0.02	0.10
Ethyl Benzene	5.99	6.37	5.42	4.18
m-Xylene	48.04	49.08	47.78	45.93
p-Xylene	21.20	20.57	20.05	20.17
o-Xylene	19.40	20.29	20.96	20.43
C ₉ PAR	0.05		0.08	
C ₉ AR	0.49	0.38	0.50	1.19
C ₁₀ + AR	0.12	0.15	0.29	0.78
Wt.% Conversion Ethyl Benzene	40.10	35.00	44.69	59.81
Mole C ₆ H ₆ /Mole Ethyl Benzene Reacted	1.02	0.86	0.85	0.96

CLAIMS:

1. A process for isomerizing xylenes mixed with ethyl benzene by contact at conversion conditions with a catalyst comprising a zeolite having a constraint index of 1 to 12, characterized in that the zeolite has a silica/alumina ratio of at least 500 and the conversion temperature is above 800°F.

2. A process according to claim 1 wherein said zeolite is ZSM-5.

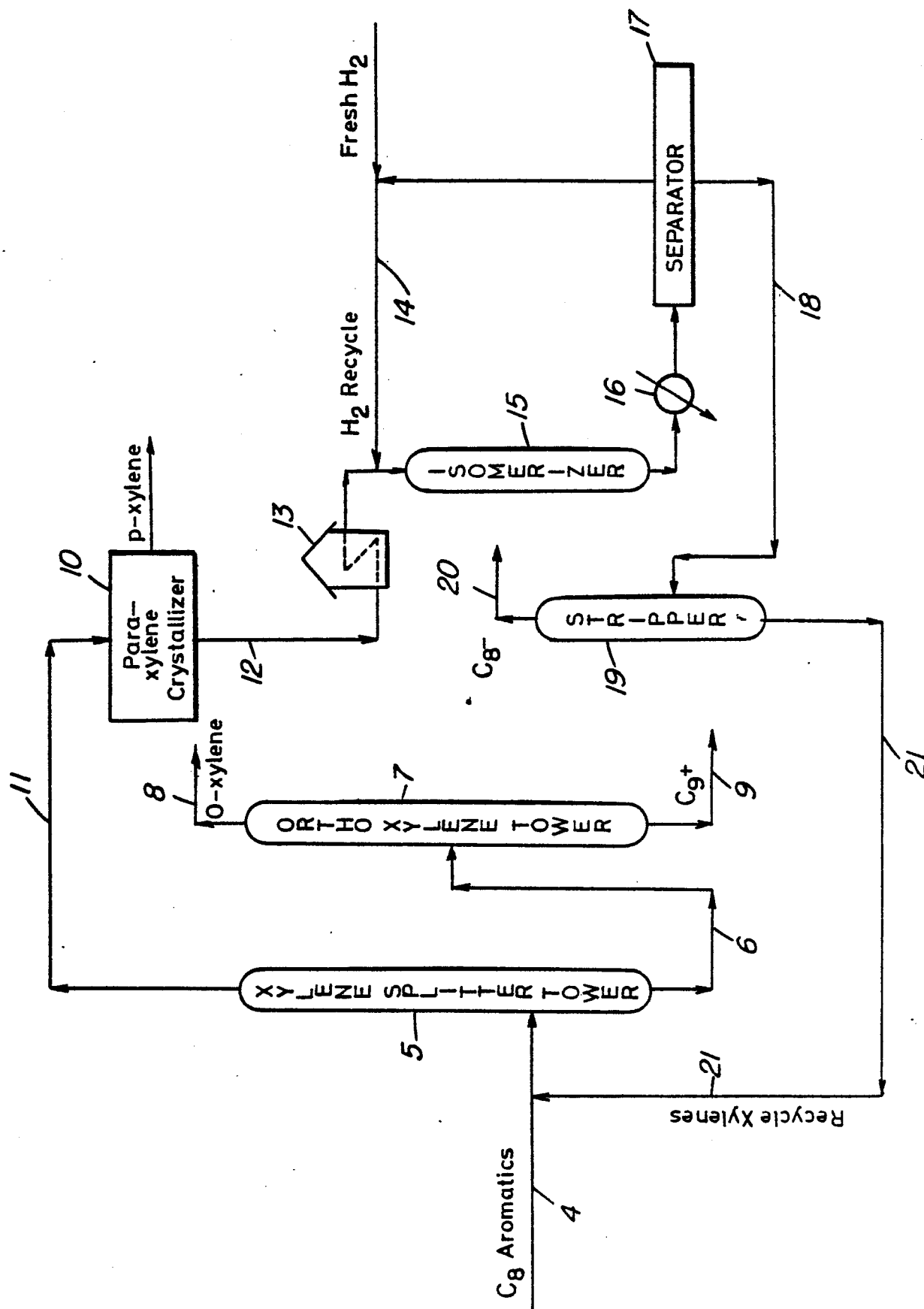
3. A process according to claim 1 wherein said zeolite is ZSM-5(ccM).

4. A process according to claim 1 or claim 3 wherein said zeolite is ZSM-5(ccPt).

5. A process according to any preceding claim wherein said zeolite constitutes from 1 to 99, preferably 5 to 80, weight percent of a composite with a binder.

6. A process according to any preceding claim which is carried out at a temperature of 800 to 1000°F.

7. A process according to any preceding claim wherein said zeolite has a silica/alumina mole ratio of 500 to 3000.





European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 78 30 0170

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	GB - A - 1 444 481 (MOBIL OIL CORPORATION) * Claims *	1-2, 5-6	C 07 C 15/08 C 07 C 5/24 C 07 C 5/30 B 01 J 29/28
			TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
			C 07 C 5/24 C 07 C 5/30 C 07 C 15/08 C 07 C 15/02 C 07 C 15/00 B 01 J 29/28 B 01 J 29/30 B 01 J 29/32 B 01 J 29/34 B 01 J 29/36
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 20-10-1978	Examiner VAN GEYT