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(54) A process for effecting catalytic isomerization of monocyclic methyl-substituted aromatic hydrocarbon compounds.

(57) A process for vapour-phase catalytic isomerization of monocyclic methyl-substituted aromatic hydrocarbon compounds of from 8 to 10 carbon atoms contained in a feedstock also containing ethylbenzene. The catalyst for the process comprises a zeolite having a constraint index of 1 to 12. The improvement in the process comprises treating the catalyst with one or more basic nitrogen compounds or precursors thereof.

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ACTORUM AG

A PROCESS FOR EFFECTING CATALYTIC ISOMERIZATION OF MONOCYCLIC METHYL-SUBSTITUTED AROMATIC HYDROCARBON COMPOUNDS.

The present invention relates to a process for the vapour-phase catalytic isomerization of monocyclic methyl-substituted aromatic hydrocarbon feedstock.

The catalytic rearrangement of alkyl groups present in alkyl aromatic hydrocarbons to provide one or more products, such as p-xylene, suitable for use in the petroleum and chemical industries has heretofore been effected by a wide variety of catalysts.

A recently developed and widely adopted catalyst for use in such processes is taught by U.S.Patent 3,856,872 to be of the ZSM-5 type of zeolite, whereby the process operates at high space velocities. Further, a process utilizing ZSM-5 type zeolites in acid form for vapor-phase conversion of a feedstock containing mixed C_8 aromatics in the absence of added hydrogen is taught by U.S.Patent 3,856,873. However, especially when the catalyst has increased acid activity, there can be a loss of xylene, the primary isomerization product, presumably due in part to disproportionation of xylenes and/or transalkylation of xylenes with any ethylbenzene which may be present in the reaction system.

The use of nitrogen compounds for various purposes in hydrocracking and reforming in the presence of catalyst other than that for use herein is known in the art. Examples of such art include U.S.Patents 2,849,377 (reforming); 3,657,110 (hydrocracking) and 3,694,345 (hydrocracking). Isomerization of alkyl aromatic compounds in the presence of nitrogen compounds to equilibrium products over catalyst other than that for use herein is taught in U.S.Patents 3,293,314 and 3,644,200. The catalyst for use in the process of U.S.Patent 3,293,314 is a solid acidic mixed metal-oxide catalyst, e.g., a silica-alumina mixture, having equilibration (tending to produce equilibrium products) and coke forming activities. Unfortunately, such catalyst materials lose their ability to maintain their equilibration tendency and, therefore, there is a decrease in desirable isomeric products as the catalysts age.

According to the present invention a process for effecting catalytic isomerization of monocyclic methyl-substituted aromatic hydrocarbon compounds of from 8 to 10 carbon atoms contained in a feedstock also containing ethylbenzene comprises contacting said feedstock in the vapor phase with a catalyst comprising a crystalline aluminosilicate zeolite having a constraint index within the range of 1 to 12, said zeolite containing hydrogen, hydrogen precursor and/or Group VIII metal cations, at a temperature of 600°F to 900°F, a pressure of 0 psig to 500 psig, a hydrogen/hydrocarbon mole ratio of 0 to 10 and a weight hourly space velocity of 0.1 to 200, said catalyst having been contacted with one or more basic nitrogen compounds or precursors therof, the resulting ratio of nitrogen atoms/aluminum atoms in the zeolite being from 0.01 to 1.0.

The preferred zeolites for use in the process are zeolites ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38: they usually constitute from 10 to 90 weight percent of a composite with a binder therefor, such as alumina.

The preferred Group VIII metal cations are nickel, iron and/or cobalt. The process is particularly applicable to the isomerisation of a feedstock which contains xylenes.

The basic nitrogen compounds or precursors thereof which are particularly favoured are ammonia, alkylamines of from 1 to 40 carbon atoms, alkyldiamines of from 2 to 40 carbon atoms, aromatics amines of from 6 to 40 carbon atoms, pyridine, pyrrolidine and aniline. Their contact with the catalyst may be effected during catalyst preparation, by periodic or continuous addition to the feedstock, by contact with the catalyst in the reactor before commencement of the process, or otherwise.

Preferred zeolites for use in the present invention are those with a SiO_2/Al_2O_3 mole ratio of at least about 12. Many are very well known. Zeolite ZSM-5, for instance,is described in U.S.Specification 3,702,886. Zeolite ZSM-11 is described in U.S.Specification 3,709 ,979. Zeolite ZSM-12 is described in U.S.Specification 3,970,544. Zeolite ZSM-35 is described in U.S. Specification 4,016,245. Zeolite ZSM-38 is described in U.S.Specification 4,046,859. The significance and definition of "Constraint Index" is also well known from extensive patent literature such as DTOS 2,438,252.

In a preferred aspect of this invention, the catalysts 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 for the present process. Therefore, the preferred catalysts 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 leat about 12 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 silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meir. 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 pyknometer 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 zeolite is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This 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:

Zeolite	Void Volume	Framework Density
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	.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

The amount of ethylbenzene in the feedstock is usually from about 5 to about 30 weight percent, more usually from about 10 to about 25 weight percent. Specific compounds contemplated for isomerisation include para-xylene, meta-xylene, ortho-xylene, mesitylene (1,3,5-trimethylbenzene) durene (1,2,4,5-tetramethylbenzene), hemimellitene (1,2,3-trimethylbenzene), pseudocumene (1,2,4-trimethylbenzene), prehnitene (1,2,3,4-tetramethylbenzene) and isodurene (1,2,3,5-tetramethylbenzene) with the xylene isomers and pseudocumene especially preferred.

The nitrogen-containing compounds useful in the present process should be ones which neither react with the charge materials nor possess catalytic activity contrary to the purpose for their use. Said nitrogen-containing compounds may be gaseous, liquid or in the form of a solid dissolved in a suitable solvent, such as, for example, toluene.

Non-limiting examples of nitrogen compounds or precursors thereof useful in this invention include, for example, ammonia, alkylamines of from 1 to about 40 carbon atoms, and preferably from 1 to about 10 carbon atoms, e.g. n-propylamine, alkyldiamines of from 2 to about 40 carbon atoms, and preferably from 6 to abouit 20 carbon atoms, aromatic amines of from 6 to about 40 carbon atoms, e.g. aniline, and heterocyclic nitrogen compounds, such as pyridine and pyrrolidine.

The catalyst may be contacted with the nitrogen compound in a variety of ways. For example, the nitrogen compound can be contacted with the catalyst during manufacture of the catalyst, prior to introducing the normal feedwtock, or it can be added to the feedstock periodically or continuously. Combinations of these modes of addition are also contemplated.

The specific examples which follow illustrate embodiments of the process of the present invention. The single Figure of the DRAWING summarises the data of Examples 2 to 4.

EXAMPLE 1

A sodium silicate solution was prepared by mixing 16 parts water and 27.7 parts sodium silicate (28.7 wt.% SiO_2, 8.9 wt.% Na_2O, 62.4% H_2O). The solution was cooled to approximately 15°C.

An acid solution was prepared by adding 1 part aluminum sulfate (17.2 wt.% Al_2O_3) to 16.4 parts water followed by 2.4 parts sulfuric acid (93 wt.% H_2SO_4) and 1.2 parts NaCl.

These solutions were mixed in an agitated vessel while 3.9 parts of NaCl were added. The gel molar ratios expressed as oxides are the following:

$$SiO_2/Al_2O_3 = 78.4$$

$$Na_2O/Al_2O_3 = 49.9$$

An organic solution was prepared by adding 1.6 parts n-propyl bromide and 3.1 parts methyl ethyl ketone to 1.9 parts tri-n-propylamine.

After the gel was heated to about 95°C, agitation was reduced and the organic solution was added above the gel. This mixture was held at about 95-110°C for 14 hours, then agitation was increased. When approximately 65% of gel was crystallized the temperature was increased to about 150-160°C and held there until crystallization was complete. Unreacted organics were removed by flashing and the remaining contents cooled.

The zeolite slurry product was diluted with 4-5 parts water per part slurry, allowed to settle and supernatent liquid was drawn off. The settled solids were reslurried to the original volume of the preceding step with water. After settling, the aqueous phase was decanted. This procedure was repeated until the sodium level of the zeolite was less than 1.0 wt.%. The washed zeolite was then filtered, dried and identified as ZSM-5 having a silica/alumina mole ratio of about 70 and a constraint index of about 8.3.

The dried zeolite was then mixed with alumina and water. It was then extruded into 1.16" pellets and dried. The extruded material contained 65 parts ZSM-5 per 35 parts alumina, by weight.

The dried extrudate was calcined for three hours at 538°C in flowing nitrogen. After cooling, the extrudate was contacted with an ammonium nitrate exchange solution (about 0.08 1b NH_4NO_3/lb extrudate) for one hour at ambient temperature. This exchange was then repeated until the sodium level was less than 0.05 wt.%. The extrudate was then contacted with a nickel nitrate exchange solution (about 0.1 lb Ni ($Ni(NO_3)_2 \cdot 6H_2O$/lb extrudate) for two hours at about 80-90°C. After this exchange, the extrudate was washed, dried and calcined in a flowing 10% air-90% nitrogen mixture at 538°C for six hours.

EXAMPLE 2

25 cc of the catalyst of Example 1 was further calcined at 1000°F in air for 24 hours and placed in an isothermal, one gallon/day reactor. Pure hydrogen was continuously passed through the reactor without recycle in order to maintain a constant molar ratio between hydrogen and hydrocarbon feedstock at the reactor inlet. A feedstock comprising the components listed in Table 2 was then passed through the reactor under the conditions listed in Table 3, hereinafter presented. Also listed in Table 3 are the results of ten separate material balances over the period of 10.5 days on stream. It will be noted that from the data generated at each material balance, an approach to equilibrium was calculated as being (weight % p-or o-isomer, respectively, of total xylenes produced - weight % of that isomer in the feed) divided by (equilibrium weight % concentration of p- or o-isomer, respectively at the reaction temperature - weight % of that isomer in feed). The p- or o-isomer equilibrium concentrations, respectively, as a function of reaction temperature may be determined according to The Chemical Thermodynamics of Organic Compounds by Stull, Westrum and Sinke, published in 1969 by Wiley

For the improved isomerization process of this invention, the zeolite is preferably employed in association with a support or binder material which acts as diluent such as, for example, a porous inorganic oxide support or a clay binder. Non-limiting examples of such binder materials include alumina, zirconia, silica, magnesia, thoria, titania, boria and combinations thereof, generally in the form of dried inorganic oxide gels and gelatinous precipitates. Suitable clay materials include, by way of example, bentonite and kieselguhr. The relative proportion of suitable cyrstalline aluminosilicate zeolite of the total composition of catalyst and binder or support may vary with the zeolite content ranging from between about 10 to about 90 percent by weight and more usually in the range of about 20 to about 80 percent by weight of the composition.

Operating conditions employed in the improved process of the present invention are important. Such conditions as temperature, pressure, space velocity, molar ratio of the reactants, hydrogen to hydrocarbon mole ration, and the presence of any feedstock diluents, such as toluene and/or C_9^+ recycle material, will have important effects on the process. Fixed or fluid bed contacting may be employed.

Within the limits of operating conditions hereinbefore set forth, the conditions of temperature and pressure adopted in practice will vary considerably depending upon equilibrium considerations and type of feed material. Optimum conditions are those in which maximum yields of desired isomer products are obtained and hence considerations of temperature and pressure will vary within a range of conversion levels designed to provide the highest selectivity and maximum yield.

TABLE 2

Feedstock Composition for Example 2

Component	Amount, wt.%
Toluene	0.04
Ethylbenzene	14.81
p-Xylene	10.07
m-Xylene	59.29
o-Xylene	15.69
C_9+ Aromatics	0.11

TABLE 3

EXAMPLE 2 - REACTION CONDITIONS AND RESULTS

Material Balance	1	2	3	4	5	6	7	8	9	10
Days on Stream	0.8	1.9	2.9	4.8	5.5	6.5	7.5	8.5	9.5	10.5
Temperature, °F	541	542	561	560	581	581	601	601	621	620
WHSV, hr.$^{-1}$	7.14	7.21	7.25	7.20	7.26	7.17	7.25	7.25	7.20	7.19
Pressure, psig	200	200	200	200	200	200	200	200	200	200
H2/HC Ratio	4.07	4.00	3.98	4.05	4.02	4.03	3.99	3.99	3.78	3.96
Ethylbenzene Conversion, mole %	3.63	3.69	6.58	6.64	11.19	11.77	17.95	18.40	26.53	26.77
Xylene Loss, mole %	.46	.49	.92	1.11	1.69	1.73	2.77	2.63	3.92	3.95
Approach to Equilibrium for p-Xylene	97.4	97.4	99.8	100.4	100.5	100.5	101.4	101.1	100.6	101.5
Approach to Equilibrium for o-Xylene	60.8	65.4	73.1	72.1	77.7	77.1	79.9	79.8	81.1	79.8
Yields, mole %										
Benzene	.43	.43	.75	.77	1.32	1.32	2.22	2.16	3.35	3.31
Toluene	.30	.33	.45	.50	.68	.68	.88	.86	1.16	1.16
Ethylbenzene	14.27	14.26	13.84	13.83	13.15	13.07	12.15	12.09	10.88	10.85
p-Xylene	20.08	20.07	20.19	20.21	20.05	20.05	19.88	19.88	19.52	19.60
m-Xylene	47.24	47.10	46.32	46.21	45.65	45.64	44.87	44.97	44.28	44.23
o-Xylene	17.33	17.46	17.75	17.68	17.91	17.88	17.94	17.96	17.91	17.85
Methylethylbenzene	.06	.08	.10	.13	.17	.18	.22	.22	.28	.29
Trimethylbenzene	.09	.08	.17	.18	.23	.26	.35	.35	.45	.47
Diethylbenzene	.11	.11	.22	.24	.40	.42	.63	.65	.83	.86
Dimethylethylbenzene	.08	.09	.21	.25	.45	.51	.84	.87	1.33	1.39

After 10.5 days on stream, the catalyst used in Example 2 was contacted in the same reactor as for Example 2 with a feedstock containing a nitrogen -containing compound, i.e., 1.10-decane diamine as indicated in Table 4, hereinafter presented. The feedstock containing the nitrogen-containing compound was pumped through the reactor for 24 hours at operating conditions of 600°F, 200 psig,a WHSV of 7 hr^{-1} and a hydrogen/hydrocarbon mole ratio of 4. The ratio of nitrogen atoms provided in the feed per aluminum atom in the zeolite component was 3.4.

Thereafter, the above feedstock without the nitrogen-containing compound was charged to the reactor and at the reaction conditions of Example 2, the catalyst was found to be inactive. The reaction temperature was increased, through increments, up to about 750°F, where a rapid reactivation of the catalyst was observed, as a result of desorption of part of the nitrogen from the catalyst, bringing the ratio of nitrogen atoms/aluminum atom in the zeolite component within the range of 0.01 to 1.0. The temperature was then reduced to 700°F where gradual recovery of catalyst activity was still observable. The reaction conditions and results from 8 material balances over the period of about 8 days on stream appear in Table 5.

TABLE 4

Feedstock Composition for Example 3 Containing a Nitrogen-Containing Compound

Component	Amount
1,10-Decane diamine	500 ppm
Toluene	0.04 wt %
Ethylbenzene	15.60 wt %
p-Xylene	11.53 wt %
m-Xylene	57.72 wt %
o-Xylene	15.02 wt %
C_9+ Aromatics	0.09 wt T

TABLE 5

EXAMPLE 3 - REACTION CONDITIONS AND RESULTS

Material Balance	11	12	13	14	15	16	17	18
Days on Stream	24.3	25.2	26.2	27.1	28.2	29.8	31.1	32.1
Temperature, °F	600	600	650	700	752	751	750	700
WHSV, hr.$^{-1}$	7.19	7.14	7.18	7.18	7.24	7.22	7.12	7.31
Pressure, psig	200	200	200	200	200	200	200	200
H2/HC Ratio	4.01	4.04	4.00	3.98	3.95	4.00	4.03	3.95
Ethylbenzene Conversion, mole %	.00	-.18	1.02	1.18	19.95	33.71	36.57	20.35
Xylene Loss, mole %	.11	.07	-.21	-.16	1.58	2.91	3.68	1.89
Activity Loss, °F	179		159	205	149	122	117	94
Approach to Equilibrium for p-Xylene	.6	.5	2.6	30.6	101.3	101.8	102.4	100.9
Approach to Equilibrium for o-Xylene	.8	-.2	-3.9	21.6	80.1	80.1	82.7	82.3
Yields, mole %								
Benzene	.00	.00	.00	.10	2.84	4.74	5.30	2.78
Toluene	.12	.06	.03	.04	.28	.55	.71	.33
Ethylbenzene	15.60	15.63	15.44	15.42	12.49	10.34	9.89	12.43
Paraxylene	11.57	11.57	11.78	14.12	19.62	19.39	19.29	19.61
Metaxylene	57.58	57.64	57.79	54.19	44.42	43.78	43.26	44.43
Orthoxylene	15.04	15.00	14.88	16.09	18.90	18.64	18.62	18.63
Propylbenzene	.08	.08	.07	.04	.00	.00	.00	.00
Methylethylbenzene	.00	.00	.00	.00	.05	.12	.17	.07
Trimethylbenzene	.02	.02	.01	.00	.08	.17	.21	.08
Diethylbenzene	.00	.00	.00	.01	.65	.97	1.02	.80
Dimethylethylbenzene	.00	.00	.00	.00	.67	1.29	1.53	.84

EXAMPLE 4

The experiment of Example 3 was continued with a feedstock composed as indicated in Table 6. The conditions for and results from 10 material balances over a period of about 10 days on stream appear in Table 7.

TABLE 6
Feedstock Composition for Example 4

Component	Amount, wt.%
Toluene	0.04
Ethylbenzene	15.20
p-Xylene	10.26
m-Xylene	59.86
o-Xylene	14.55
C_9^+ Aromatics	0.08

TABLE 7

EXAMPLE 4 - REACTION CONDITIONS AND RESULTS

Material Balance	19	20	21	22	23	24	25	26	27	28
Days on Stream	34.1	36.1	37.1	38.1	39.1	40.1	41.1	42.1	43.1	44.8
Temperature, °F	700	701	701	701	700	700	700	700	700	700
WHSV, hr.$^{-1}$	7.19	7.22	7.22	7.21	7.22	7.22	7.25	7.14	7.12	7.19
Pressure, psig	200	200	200	200	200	200	200	200	200	200
H2/HC Ratio	3.97	3.86	3.92	3.93	3.93	3.93	3.91	3.98	3.97	3.94
Ethylbenzene Conversion, mole %	20.41	21.75	22.42	23.04	23.32	23.49	23.93	24.12	24.88	25.34
Xylene Loss, mole %	1.86	1.84	1.99	1.92	2.00	1.88	2.03	2.13	2.01	2.15
Activity Loss, °F	96	94	92	91	90	89	89	88	87	86
Approach to Equilibrium for p-Xylene	101.1	100.8	101.2	100.7	100.9	100.3	100.9	101.6	100.5	100.9
Approach to Equilibrium for o-Xylene	81.4	81.5	81.1	80.1	76.5	84.9	82.7	82.8	79.1	78.6
Yields, mole %										
Benzene	2.67	2.84	2.96	3.03	3.00	3.04	3.17	3.10	3.19	3.43
Toluene	.33	.35	.36	.36	.36	.37	.38	.41	.40	.42
Ethylbenzene	12.10	11.90	11.79	11.70	11.66	11.63	11.57	11.54	11.42	11.35
Paraxylene	19.75	19.72	19.72	19.69	19.70	19.66	19.69	19.74	19.66	19.67
Metaxylene	44.77	44.79	44.72	44.84	44.98	44.65	44.64	44.52	44.88	44.80
Orthoxylene	18.59	18.60	18.55	18.51	18.30	18.77	18.62	18.61	18.43	18.38
Methylethylbenzene	.07	.07	.07	.07	.07	.07	.08	.08	.08	.08
Trimethylbenzene	.09	.09	.10	.09	.16	.10	.10	.11	.10	.11
Diethylbenzene	.77	.78	.83	.81	.84	.83	.83	.90	.85	.85
Dimethylethylbenzene	.86	.85	.89	.90	.93	.88	.92	.99	.99	.92

In the single figure of the drawing ethylbenzene conversion is plotted against xylene loss for the results of Example 2, Example 3 and Example 4. It is readily observed that at a particular ethylbenzene conversion, the process of the present invention, whereby the catalyst has been treated with a nitrogen-containing compound, exhibits substantially reduced xylene loss. This reduction in xylene loss for isomerization of xylenes is an unexpected and significant benefit and indicates that, whatever the monocyclic methyl-substituted aromatic hydrocarbon feedstock may be, substantial reduction in primary product losses will be effected and selectivity to desired product isomer will be enhanced.

EXAMPLE 5

A catalyst prepared as in Example 1, but not contacted with the nickel nitrate solution, was placed in the reactor used in Examples 2-4. A feedstock composed as described in Table 8 was then passed through the reactor at 25 psig, 600°F, a WHSV of 5 hr^{-1} and a hydrogen/hydrocarbon mole ratio of 0 (absence of added hydrogen). The results of this experiment are presented in Table 9.

EXAMPLE 6

The feedstock for Example 5 is then injected with ammonia to the extent that the ratio of nitrogen atoms/aluminum atom in the zeolite is 0.1. The injection of ammonia into the feedstock is stopped after a time and the reaction temperature is increased to 750°F. Results of this experiment are also presented in Table 9 for comparison with the results from Example 5.

TABLE 8

Feedstock Composition for Example 5

Component	Amount, wt. %
Toluene	0.9
Ethylbenzene	6.9
p-Xylene	10.5
m-Xylene	62.9
o-Xylene	18.7
C_9^+ Aromatics	-

TABLE 9

Results from Examples 5 and 6

Example	5	6
Ethylbenzene Conversion, Wt. %	24.6	24.6
Xylene Loss, wt. %	1.84	0.87
Approach to Equilibrium for p-xylene	102.8	102.0
Yield, wt. %		
C_1-C_5 hydrocarbons	-	0.1
Benzene	0.7	1.2
Toluene	1.7	1.1
Ethylbenzene	5.2	5.2
p-Xylene	21.9	21.7
m-Xylene	49.0	48.6
o-Xylene	19.5	21.0
C_9^+ Aromatics	2.0	1.1

CLAIMS:

1. A process for effecting catalytic isomerization of monocyclic methyl-substituted aromatic hydrocarbon compounds of from 8 to 10 carbon atoms contained in a feedstock also containing ethylbenzene which comprises contacting said feedstock in the vapor phase with a catalyst comprising a crystalline aluminosilicate zeolite having a constraint index within the range of 1 to 12, said zeolite containing hydrogen,hydrogen precursor and/or Group VIII metal cations, at a temperature of 600°F to 900°F, a pressure of 0 psig to 500 psig, a hydrogen/hydrocarbon mole ratio of 0 to 10 and a weight hourly space velocity of 0.1 to 200, said catalyst having been contacted with one or more basic nitrogen compounds or precursors thereof, the resulting ratio of nitrogen atoms/aluminum atoms in the zeolite being from 0.01 to 1.0.

2. A process according to Claim 1 wherein said zeolite is ZSM-5, ZSM-11, ZSM-12, ZSM-35 or ZSM-38.

3. A process according to Claim 1 or Claim 2 wherein said zeolite constitutes from 10 to 90 weight percent of a composite with a binder therefor.

4. A process according to Claim 3 wherein said binder is alumina.

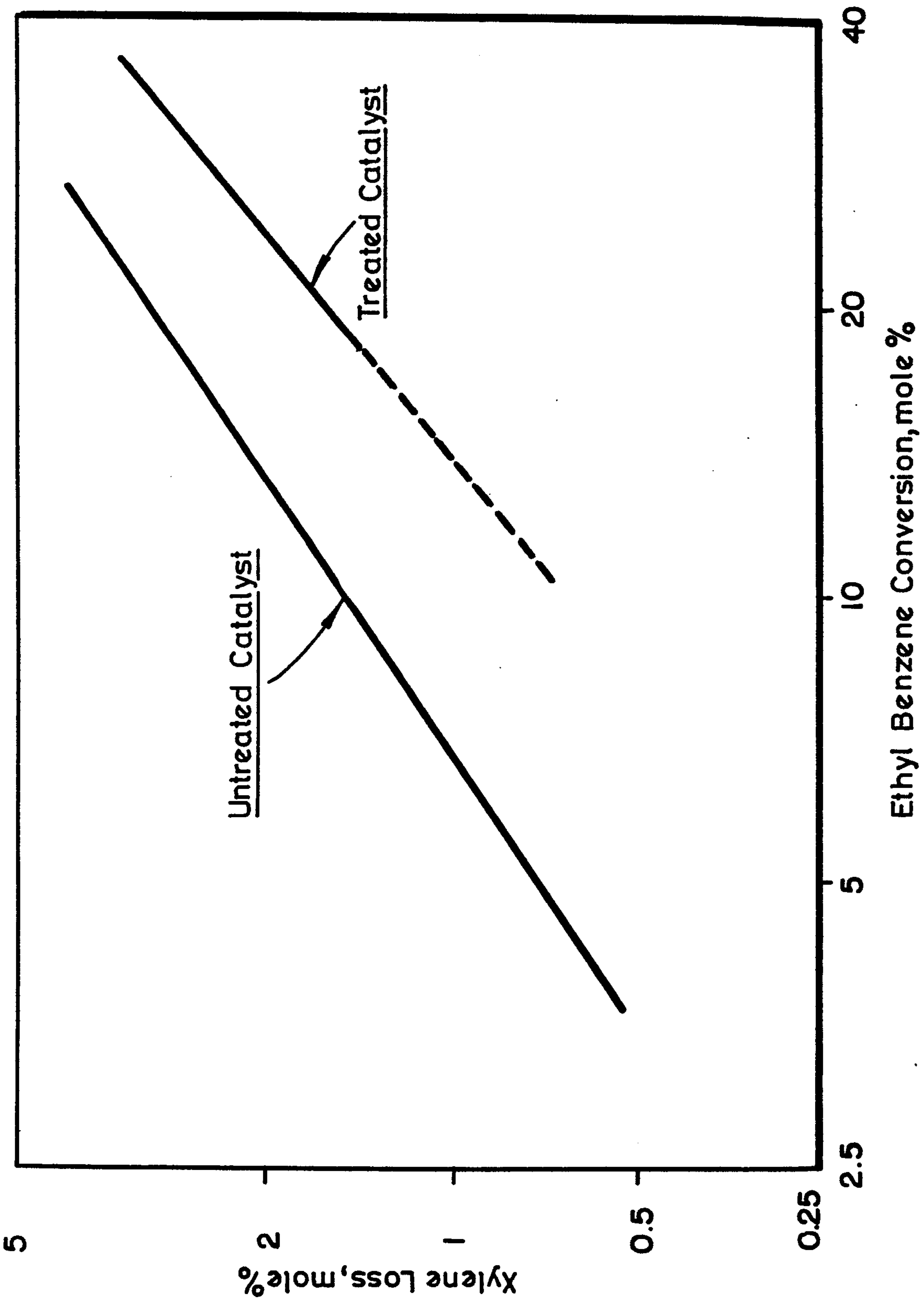
5. A process according to any preceding claim wherein said Group VIII metal cations are nickel, iron and/or cobalt.

6. A process according to any preceding claim wherein said feedstock contains xylenes.

7. A process according to any preceding claim wherein said basic nitrogen compounds or precursors thereof are selected from ammonia, alkylamines of from 1 to 40 carbon atoms, alkyldiamines of from 2 to 40 carbon atoms, aromatics amines of from 6 to 40 carbon atoms, pyridine, pyrrolidine and aniline.

8. A process according to any preceding claim wherein the contact of the nitrogen compound with the catalyst is effected during catalyst preparation.

9. A process according to any of Claims 1 to 8 wherein the contact of the nitrogen compound with the catalyst is effected by periodic or continuous addition of that compound to the feedstock.


Treated Catalyst
Untreated Catalyst
Ethyl Benzene Conversion, mole %
2.5
5
10
20
40
Xylene Loss, mole %
0.25
0.5
1
2
5

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EUROPEAN SEARCH REPORT

Application number
EP 78 30 0119

0000432

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	US - A - 3 856 872 (R.A.MORRISON) * Column 7; claims * --	1-6
	US - A - 3 992 466 (C.J.PLANK et al.) * Columns 5-6 * --	1-6
A	DE - A - 2 558 035 (MOBIL OIL CORP.) * Claims * ----	1-4, 7,9

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 07 C 15/02
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 5/22
C 07 C 5/30
C 07 C 15/00
C 07 C 15/02
C 07 C 15/08
B 01 J 29/28
B 01 J 29/30
B 01 J 29/32
B 01 J 29/34
B 01 J 29/06

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	Date of completion of the search	Examiner
The Hague	10-10-1978	VAN GEYT