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SELECTIVE PARA-XYLENE PRODUCTION BY TOLUENE METHYLATION

This invention relates to a process for the selective production of para-xylene by catalytic methylation of toluene in the presence of a solid catalyst.

5 Alkylation of aromatic hydrocarbons utilizing crystalline aluminosilicate catalysts has heretofore been described. U.S. Patent No. 2,904,607 to Mattox refers to alkylation of aromatic hydrocarbons with an olefin in the presence of a crystalline metallic aluminosilicate having
10 uniform pore openings of about 6 to 15 Angstrom units. U.S. Patent No. 3,251,897 to Wise describes alkylation of aromatic hydrocarbons in the presence of X- or Y-type crystalline aluminosilicate zeolites, specifically such type zeolites wherein the cation is rare earth and/or
15 hydrogen. U.S. Patent No. 3,751,504 to Keown et al. and U.S. Patent No. 3,751,506 to Burress describe vapor phase alkylation of aromatic hydrocarbons with olefins, e.g. benzene with ethylene, in the presence of a ZSM-5 type zeolite catalyst.

20 The alkylation of toluene with methanol in the presence of a cation exchanged zeolite Y has been described by Yashima et al. in the Journal of Catalysis 16, 273-280 (1970). These workers reported selective production of para-xylene over the approximate
25 temperature range of 200° to 275°C, with the maximum yield of para-xylene in the mixture of xylenes, i.e. about 50 percent of the xylene product mixture, being observed at 225°C. Higher temperatures were reported to result in an increase in the yield of meta-xylene and a
30 decrease in production of para and ortho-xylenes.

Of the xylene isomers, e.g. ortho-, meta- and para-xylene, the latter is of particular value being useful in the manufacture of terephthalic acid which is an intermediate in the manufacture of synthetic fibers such
35 as Dacron brand fiber available from the DuPont de Nemours Company of Wilmington, Delaware. Mixtures of

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xylylene isomers either alone or in further admixture with ethylbenzene, generally containing a concentration of about 24 weight percent para-xylylene in the equilibrium mixture, have been previously separated by expensive
5 superfraction and multistage refrigeration steps. Such process, as will be realized, has involved high operation costs and has a limited yield.

U.S. Patents 3,965,209 to Butter et al. and 4,067,920 to Kaeding teach processes for producing para-
10 xylylene in low conversion and high yield by reaction of toluene with methanol. The reaction is exothermic, generating about 16.5 kcal/mol (280 Btu/lb) of para-xylylene produced.

The use of steam co-feed (U.S. Patents 4,935,574 and
15 4,843,057 to D'Amore et al.) or interstage methanol addition (U.S. Patent 4,761,513 to Steacy) have been disclosed as means to quench the reaction exotherm and to improve operability of a fixed-bed process.

Under typical reaction conditions the process is
20 also prone to rapid catalyst deactivation. The use of hydrogen co-feed (U.S. Patent 4,444,989 to Herkes) has been disclosed to reduce coking. Kaeding (U.S. Patents 4,067,920 and 4,158,024 to Kaeding) discloses the use of a fluidized catalyst zone but with no teaching of
25 preferred fluidization conditions.

U.S. Patent 4,001,346 to Chu relates to a process for the selective production of para-xylylene by methylation of toluene in the presence of a catalyst comprising a crystalline aluminosilicate zeolite which
30 has undergone prior treatment to deposit a coating of between about 15 and about 75 weight percent of coke thereon.

U.S. Patent 4,097,543 to Haag et al. relates to a process for the selective production of para-xylylene (up
35 to about 77%) by disproportionation of toluene in the presence of a crystalline aluminosilicate catalyst which has undergone precoking to deposit a coating of at least about 2 weight percent coke thereon.

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U.S. Patent 4,554,394 to Forbus and Kaeding teach the use of phosphorus-treated zeolite catalysts for enhancing para-selectivity in aromatics conversion processes. U.S. Patent 4,623,633 to Young relates to the use of thermal shock calcination of aluminosilicates to produce up to 66% para-xylene selectivity.

Summary of the Invention

The invention provides a process for the selective production of para-xylene which comprises reacting toluene with a methylating agent in the presence of a catalyst comprising a microporous material having a Constraint Index, measured prior to selectivation, of from about 1 to about 12, which catalyst has been selectivated by the steps of:

(a) presteaming the catalyst at a temperature of from about 800°C to about 1050°C for at least about 10 minutes;

(b) depositing from about 1 to about 20 weight percent of coke on said catalyst; and

(c) continuously controlling the weight percent of coke on said catalyst at from about 1 to about 20 weight percent.

The present invention improves selectivity and yield in a process for producing para-xylene from toluene by steaming and precoking the catalyst under controlled conditions, and then continuously controlling the degree of coke loading during process operation. The order of the steaming and precoking steps is critical in the present invention, as is the severity of both steps. These two steps in sequence enable the process of the present invention to provide unusually high selectivity for para-xylene at commercially useful toluene conversions of 5 weight percent or more per pass, typically 7 weight percent or more per pass. Para-xylene selectivities typically exceed 90 weight percent in the present process, and preferably exceed 94 weight percent. Conversion conditions typically include temperature

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between about 300° and about 750°C, preferably between about 500° and about 700°C, pressure of between about 1 atmosphere and 1000 psig, weight hourly space velocity of between about 0.5 and 1000, and a molar ratio of
5 methylating agent to toluene (in the reactor charge) of less than about 5, more typically from about 0.05 to about 5.

Suitable catalyst presteaming temperatures range from about 800°C to about 1050°C, preferably from about
10 900° to about 1040°C, while the presteaming contact time ranges from about 10 minutes to several hundred hours, more typically up to about 100 hours. Higher steaming temperatures may irreversibly degrade the catalyst, causing its catalytic activity for toluene methylation to
15 decrease below a commercially useful level.

Additionally, the catalyst may be selectivated by treatment with one or more elements such as Si, P, Mg, or B. Phosphorus-treated zeolites are taught in U.S. Patent 4,554,394 to Forbus and Kaeding, cited above, which is
20 incorporated by reference as if set forth at length herein for the method of depositing such elements on the catalyst.

The term "coke loading" is used herein in terms of weight percent to refer to the amount of coke deposited
25 on the catalyst as a percentage of the total weight of the composite catalyst. For example, a 100 gram catalyst sample having coke loading of 5 weight percent would contain 5 grams of coke and 95 grams of composite catalyst.

30 The process of the present invention is preferably carried out in a fluid bed or moving bed reactor so that the extent of coke loading can be controlled by varying the severity and/or the frequency of continuous oxidative regeneration in the catalyst regenerator.

35 Coke deposited on the catalyst during normal processing is partially removed by regeneration. The amount of coke left on the catalyst after regeneration may be controlled to balance the desired para-xylene

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selectivity against catalyst activity. Generally, more severe and/or more frequent regenerations remove more coke from the catalyst and less severe and/or less frequent regenerations remove less coke from the catalyst.

The catalyst decoking step of the present invention is continuously controlled to enable the operator to maintain the desired para-xylene selectivity, or to adjust the para-xylene selectivity and toluene conversion as required.

Generally, precoking of the catalyst will be accomplished by initially utilizing the uncoked catalyst in the toluene methylation reaction, during which coke is deposited on the catalyst surface and thereafter controlled within the above-noted range of from about 1 to about 20 weight percent (preferably from about 1 to about 15 weight percent, more preferably from about 1 to about 10 weight percent, and most preferably from about 1 to about 5 weight percent) by periodic regeneration by exposure to an oxygen-containing atmosphere at an elevated temperature.

One of the advantages of the preselectivated catalyst described herein is its ease of regenerability. Thus, after the preselectivated catalyst accumulates additional coke as it catalyzes the toluene methylation reaction, it can easily be regenerated by burning off a controlled amount of coke in the partial combustion atmosphere of the regenerator at temperatures in the range of from about 400° to about 700°C. The coke loading on the catalyst is thereby reduced in the regenerator, but not eliminated, so that the regenerated catalyst returning to the toluene methylation reaction zone is coke-loaded at a level of from about 1 to about 20 weight percent, more typically in the range of from about 1 to about 5 weight percent.

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Catalysts

The members of the class of microporous materials useful as catalysts in the present invention have an effective pore size of generally from about 5 to about 8 Angstroms or larger, such as to freely sorb normal hexane. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the microporous crystalline material is not of the desired type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering of the rings or pore blockage may render these microporous materials ineffective.

Although 12-membered rings in theory would not offer sufficient constraint to produce advantageous conversions, it is noted that the puckered 12-ring structure of TMA offretite does show some constrained access. Other 12-ring structures may exist which may be operative for other reasons, and therefore, it is not the present intention to entirely judge the usefulness of the particular microporous crystalline material solely from theoretical structural considerations.

A convenient measure of the extent to which a microporous crystalline solid provides control to molecules of varying sizes to its internal structure is the Constraint Index of the solid. The method by which the Constraint Index is determined is described in U.S. Patent Number 4,016,218, incorporated herein by reference for details of the method. U.S. Patent Number 4,696,732 discloses Constraint Index values for typical materials and is incorporated by reference as if set forth at length herein.

In a preferred embodiment, the catalyst contains a zeolite having a Constraint Index, measured prior to

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selectivation, of between about 1 and about 12. Examples of such zeolite catalysts include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, and MCM-22, with ZSM-5 and ZSM-11 being particularly preferred.

5 Zeolite ZSM-5 and the conventional preparation thereof are described in U.S. Patent Number 3,702,886, the disclosure of which is incorporated herein by reference. Other preparations for ZSM-5 are described in U.S. Patent Numbers Re. 29,948 (highly siliceous ZSM-5);
10 4,100,262 and 4,139,600, the disclosure of these is incorporated herein by reference. Zeolite ZSM-11 and the conventional preparation thereof are described in U.S. Patent Number 3,709,979, the disclosure of which is incorporated herein by reference. Zeolite ZSM-12 and the
15 conventional preparation thereof are described in U.S. Patent Number 3,832,449, the disclosure of which is incorporated herein by reference. Zeolite ZSM-23 and the conventional preparation thereof are described in U.S. Patent Number 4,076,842, the disclosure of which is
20 incorporated herein by reference. Zeolite ZSM-35 and the conventional preparation thereof are described in U.S. Patent Number 4,016,245, the disclosure of which is incorporated herein by reference. Another preparation of ZSM-35 is described in U.S. Patent Number 4,107,195, the
25 disclosure of which is incorporated herein by reference. ZSM-48 and the conventional preparation thereof is taught by U.S. Patent 4,375,573, the disclosure of which is incorporated herein by reference.

MCM-22 is disclosed in U.S. Patents 5,304,698 to
30 Husain, 5,250,277 to Kresge et al., 5,095,167 to Christensen, and 5,043,503 to Del Rossi et al., which patents are incorporated by reference as if set forth at length herein.

Additional molecular sieves which find utility in
35 conjunction with the present invention include pillared silicates and/or clays; aluminophosphates, e.g. ALPO-5, VPI-5; silicoaluminophosphates, e.g. SAPO-5, SAPO-37, SAPO-31, SAPO-40, SAPO-41; and other metal

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aluminophosphates. These are variously described in U.S. Patents 4,440,871; 4,554,143; 4,567,029; 4,666,875; and 4,742,033. The layered material MCM-36, as described in U.S. Patent 5,304,698 to Husain, is also useful in the present invention.

Many composite catalysts can be modified or selectivated to improve para-xylene yields from toluene alkylation. For example, U.S. Patent 3,965,209 to Butter et al. teaches a method for steaming a catalyst containing a medium-pore zeolite to improve its para-xylene selectivity. U.S. Patent 4,158,024 to Kaeding et al. teaches a method for improving the para-xylene selectivity of a toluene alkylation process by adding at least 0.5 weight percent magnesium to the catalyst which contains a medium-pore zeolite. U.S. Patent 4,554,394 to Forbus et al. teaches a method for treating modified ZSM-5 zeolite-containing catalysts with a vapor phase organophosphorus reagent such as trimethylphosphite or dimethylmethylphosphonate in order to improve the para-selective properties of such catalysts for the conversion of aromatic materials.

Examples

Example 1

A fluidizable catalyst containing ZSM-5 was calcined at 538°C (1000°F) for 3 hours to remove residual volatile material and then steamed at 1025°C (1877°F) for 4 hours at 101 kPa (0 psig) steam. Toluene and methanol in a molar ratio of 4/1 was passed over 40 grams of catalyst in a fluidized bed of catalyst operated below the transport velocity at reaction conditions of 597°C (1107°F), 3.5 WHSV, and 232 kPa (19 psig). The reactor was operated in a batch mode with respect to catalyst for a period of 11 hours. A two-phase liquid product consisting of a hydrocarbon phase and an aqueous phase was sampled at different times during the run and analyzed. The hydrocarbon phase contained the desired xylene product rich in para-xylenes. At the end of the

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run the catalyst was purged with nitrogen and the reactor cooled and a sample of catalyst removed and analyzed for coke content. The composition of the hydrocarbon phase (Table 1) shows a para-selectivity (para/para+meta+ortho) of 93.9% for a catalyst containing 4.97 wt.% coke and not exposed to cyclic hydrocarbon process/regeneration cycles.

Example 2

A sample of the steamed fluidizable catalyst described in Example 1 was loaded into a fluid bed reactor. A mixture of toluene and methanol in a toluene/methanol molar ratio of 4/1 was passed over the catalyst at reaction conditions of 599°C (1110°F), 1.0 WHSV, and 101 kPa (0 psig). The reactor was operated under cyclic hydrocarbon process/regeneration conditions with respect to catalyst. A cycle consisted of processing toluene/methanol feed for 6 or 12 hours, followed by a nitrogen purge for 30 minutes during which time the catalyst bed was cooled to 552°C (1025°F), followed by an air regeneration for 2 hours at 552°C (1025°F), followed by a nitrogen purge for 30 minutes during which time the catalyst bed was reheated to 599°C (1110°F) for the next hydrocarbon cycle. A two-phase liquid product consisting of a hydrocarbon phase and an aqueous phase was sampled at the end of the hydrocarbon cycle and analyzed. The hydrocarbon phase contained the desired xylene product rich in para-xylenes. After 8 cycles a sample of catalyst was removed from the reactor, dried at 79°C (175°F) in air for 1.5 hours to remove residual adsorbed hydrocarbon, and analyzed for coke content. The composition of the hydrocarbon phase (Table 2) shows that the para-xylene selectivity increased to 98% during the cyclic treatment. After 8 cycles, the catalyst contained less coke than Example 1 but was producing para-xylene in higher selectivity.

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Table 1

	<u>Example 1</u>
Reaction Conditions	
Temperature, °C (°F)	597 (1107)
Feed WHSV	3.5
Pressure, kPa (psig)	232 (19)
Toluene/Methanol (mol)	4
Cycle #	1
Time on Stream, hrs	10
Hydrocarbon Phase Composition, wt. %	
C ₃ -	0.07
C ₆ /C ₇ PON	0.19
Benzene	0.10
Toluene	84.58
Ethyl Benzene	0.04
o-Xylene	0.31
m-Xylene	0.56
p-Xylene	13.42
Methyl Ethyl Benzenes	0.15
Trimethyl Benzenes	0.38
C ₁₀ + Aromatics	0.20
Total Hydrocarbon Stream Time, hrs.	11.25
Coke on Catalyst, wt. %	4.97
Toluene conversion, wt. %	12.5
Para-xylene selectivity, wt. %	93.9

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Table 2

	Ex. 2			
Reaction Conditions				
Temperature, °C (°F)	599 (1110)			
Feed WHSV	1.0			
Pressure, psig	0			
Toluene/Methanol (mol)	4			
Cycle #	2	4	6	8
Time on Stream, hrs.	13	12	12	12
Hydrocarbon Phase Composition, wt.%				
C ₅ -	0.10	0.13	0.10	0.14
C ₆ /C ₇ PON	0.04	0.09	0.11	0.12
Benzene	0.16	0.11	0.08	0.07
Toluene	82.34	85.39	88.32	90.01
Ethyl Benzene	0.03	0.03	0.03	0.03
o-Xylene	0.32	0.14	0.07	0.06
m-Xylene	0.71	0.28	0.14	0.12
p-Xylene	15.61	13.40	10.86	9.20
Methyl Ethyl Benzenes	0.12	0.10	0.08	0.07
Trimethyl Benzenes	0.37	0.18	0.10	0.08
C ₁₀ +	0.20	0.15	0.11	0.10
Cumulative Hydrocarbon Stream Time, hrs.	21	39	57	75
Coke on Catalyst, wt.%	--	--	--	3.82
Toluene conversion, wt.%	15.5	12.4	9.4	7.6
Para-xylene selectivity, wt.%	93.8	97.0	98.1	98.1

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Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended

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claims.



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What is claimed is:

1. A process for the selective production of para-xylene which comprises reacting toluene with a methylating agent in the presence of a catalyst
5 comprising a microporous material having a Constraint Index, measured prior to selectivation, of from about 1 to about 12, which catalyst has been selectivated by the steps of:
 - 10 (a) presteaming the catalyst at a temperature of at least about 800°C for at least about 10 minutes;
 - (b) depositing from about 1 to about 20 weight percent of coke on said catalyst; and
 - (c) continuously controlling the weight percent of coke on said catalyst at from about 1 to about 20 weight
15 percent.
2. The process of claim 1 wherein said methylating agent is methanol, methylchloride, methylbromide, dimethylether or dimethylsulfide.
3. The process of claim 1 wherein the step of
20 reacting toluene with a methylating agent is carried out at a temperature between about 300° and 750°C, a pressure of between about 1 atmosphere and 1000 psig, a weight hourly space velocity between about 0.5 and about 1000 employing a molar ratio of methylating agent to toluene
25 of less than about 5.
4. The process of claim 1 wherein said catalyst contains a crystalline aluminosilicate zeolite characterized by a silica/alumina ratio in excess of 30.
5. The process of claim 4 wherein said crystalline
30 aluminosilicate zeolite has the structure of ZSM-5.
6. The process of claim 1 wherein said catalyst has undergone prior treatment with a steam-containing atmosphere at a temperature between about 800°C to about 1050°C for between about 10 minutes and about 100 hours.
- 35 7. The process of claim 6 wherein said catalyst contains a crystalline aluminosilicate having the structure of ZSM-5.



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8. The process of claim 6 wherein said methylating agent is methanol.

5 9. The process of claim 6 wherein the step of reacting toluene with a methylating agent is carried out at a temperature between about 300° and about 750°C, a pressure of between about 1 atmosphere and 1000 psig, a weight hourly space velocity of between about 0.5 and 1000, employing a molar ratio of methylating agent to toluene of from about 0.05 to about 5.

10. The process of claim 9 wherein said temperature is between about 500° and about 700°C.

11. The process of claim 9 wherein said methylating agent is methanol present in an amount corresponding to a methanol/toluene molar ratio between about 0.1 and about 2.

12. The process of claim 1 further comprising reacting a mixture of toluene and a methylating agent in the presence of said catalyst to convert at least 5 weight percent of said toluene per pass to a product mixture containing at least about 90 weight percent para-xylene.

13. The process of claim 12 further comprising converting at least 7 weight percent of said toluene per pass to a product mixture containing at least about 90 weight percent para-xylene.

14. The process of claim 12 further comprising converting at least 5 weight percent of said toluene per pass to a product mixture containing at least about 94 weight percent para-xylene.

15. The process of claim 12 further comprising continuously regenerating said catalyst under oxidation conditions to provide a catalyst coke loading level of from about 1 to about 15 weight percent.

16. The process of claim 15 further comprising continuously regenerating said catalyst under oxidation conditions to provide a para-xylene selectivity of at least about 94 weight percent.