

SHAPE SELECTIVE HYDROCARBON CONVERSION

The present invention is directed to shape selective hydrocarbon conversion such as the selective production of para-substituted aromatic compounds and in particular the selective disproportionation of toluene to produce para-xylene.

The term shape-selective catalysis describes unexpected catalytic selectivities in zeolites. The principles behind shape selective catalysis have been reviewed extensively, e.g. by N.Y. Chen, W.E. Garwood and F.G. Dwyer, "Shape Selective Catalysis in Industrial Applications, 36, Marcel Dekker, Inc. (1989). Within a zeolite pore, hydrocarbon conversion reactions such as paraffin isomerization, olefin skeletal or double bond isomerization, oligomerization and aromatic disproportionation, alkylation or transalkylation reactions are governed by constraints imposed by the channel size. Reactant selectivity occurs when a fraction of the feedstock is too large to enter the zeolite pores to react; while product selectivity occurs when some of the products cannot leave the zeolite channels. Product distributions can also be altered by transition state selectivity in which certain reactions cannot occur because the reaction transition state is too large to form within the zeolite pores or cages. Another type of selectivity results from configurational diffusion where the dimensions of the molecule approach that of the zeolite pore system. A small change in dimensions of the molecule or the zeolite pore can result in large diffusion changes leading to different product distributions. This type of shape selective catalysis is demonstrated, for example, in selective toluene disproportionation to p-xylene.

Para-xylene may be produced by methylation of toluene with methanol as described by Chen et al., J. Amer. Chem. Sec. 1979, 101, 6783, and by toluene disproportionation, as described by Pines in "The Chemistry of Catalytic

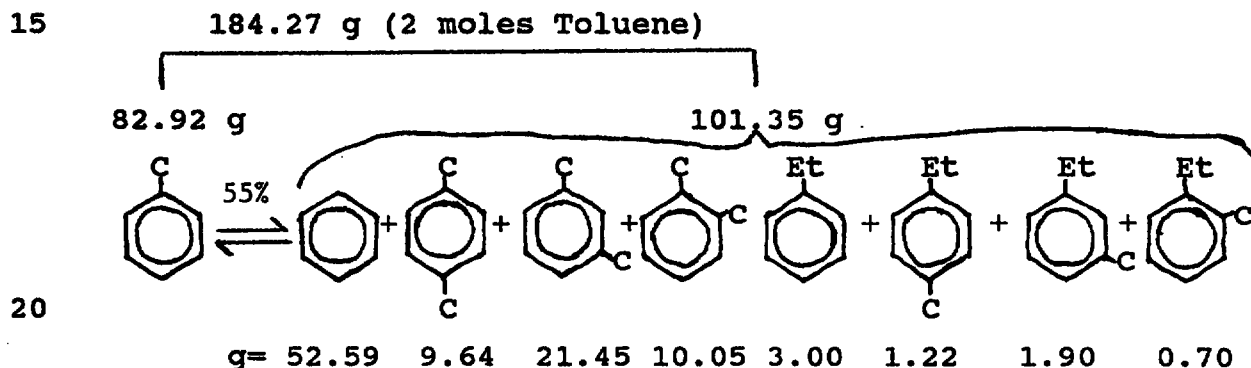


Hydrocarbon Conversions", Academic Press, N.Y., 1981, p. 72. Such methods typically result in the production of a mixture including para-xylene, ortho-xylene, and meta-xylene. Depending upon the para-selectivity of the catalyst and the reaction conditions, different percentages of para-xylene are obtained. The yield, i.e., the amount of feedstock actually converted to xylene, is also affected by the catalyst and the reaction conditions.

Previously known toluene methylation reactions typically provide many by-products such as those indicated in the following formula:

Thermodynamic Equilibria for Toluene Conversion
to the Products Indicated

Non-MTPX



$$\text{Yield} = \text{Selectivity} \times \text{Conversion} = \frac{100 \times 9.64}{101.35} \times 0.55 = 5.23 \text{ wt\%}$$

$$\text{p-Xylene Yield} = 100 \times \frac{9.64}{184.27} = 5.23 \text{ wt\%}$$

$$\text{p-Xylene Purity (p-Xylene/all C}_8\text{'s)} = 21.45 \text{ wt\%}$$

One method for increasing para-selectivity of zeolite catalysts is to modify the catalyst by treatment with "selectivating agents". Various silicon compounds have been used to modify catalysts to improve selectivity in hydrocarbon conversion processes. For example, U.S. Patent

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hydrocarbon conversion processes. For example, U.S. Patent Nos. 4,145,315, 4,127,616, and 4,090,981 describe the use of a silicone compound dissolved in an organic solvent to treat a zeolite. U.S. Patent Nos. 4,465,886 and 4,477,583 describe the use of an aqueous emulsion of a silicone to treat a zeolite. U.S. Patent Nos. 4,950,835 and 4,927,979 describe the use of alkoxysilanes carried by gases or organic solvents to treat a zeolite. U.S. Patent Nos. 4,100,215 and 3,698,157 describe the use of silanes in hydrocarbons, e.g., pyridine, ethers, to treat a zeolite. Such modification methods are known in the art to be carried out after agglomeration of the zeolite.

Some of these catalyst modification procedures, for example, U.S. Patent Nos. 4,477,583 and 4,127,616 have been successful in obtaining para-selectivity, i.e., para-xylene/all xylenes, of greater than about 90% but with commercially unacceptable toluene conversions of only about 10%, resulting in a yield of not greater than about 9%, i.e., 10% x 90%. Such processes also produce significant quantities of ortho-xylene and meta-xylene thereby necessitating expensive separation processes in order to separate the para-xylene from the other isomers.

Typical separation procedures comprise costly fractional crystallization and adsorptive separation of para-xylene from other xylene isomers which are customarily recycled. Xylene isomerization units are then required for additional conversion of the recycled xylene isomers into an equilibrium mixture comprising para-xylene.

Those skilled in the art appreciate that the expense of the separation process is proportional to the degree of separation required. Therefore, significant cost savings are achieved by increasing selectivity to the para-isomer while maintaining commercially acceptable conversion levels.

It is, therefore, highly desirable to provide a highly selective process for the production of para-xylene from

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toluene while maintaining commercially acceptable toluene conversion levels. It is also highly desirable to provide an efficient and economical method for selectivating the catalyst employed.

5 Accordingly, the invention resides in one aspect in a catalyst comprising a crystalline molecular sieve having a Constraint Index of 1-12 which has been preselectivated by agglomerating a mixture comprising crystalline molecular
10 sieve and an organosilicon compound and then calcining the resultant agglomerate.

 In a further aspect, the invention resides in a process for shape selective hydrocarbon conversion, such as the para-selective disproportionation of toluene, comprising contacting a hydrocarbon feedstock with a
15 catalyst comprising a crystalline molecular sieve having a Constraint Index of 1-12 which has been preselectivated by agglomerating a mixture comprising crystalline molecular sieve and an organosilicon compound and then calcining the resultant agglomerate.

20 The present invention is useful in shape selective hydrocarbon conversion processes such as in converting various aromatics of C_{6-12} e.g., toluene and benzene, to commercially useful para-substituted benzenes, such as para-xylene.

25 Molecular sieves to be used in the process of the invention include intermediate pore zeolites. Such medium pore zeolites have a Constraint Index from 1 to 12. The method by which Constraint Index is determined is described fully in U.S. Patent No. 4,016,218. Molecular sieves which
30 conform to the specified values of Constraint Index for intermediate pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, MCM-22, and Zeolite Beta which are described, for example, in U.S. Patent Nos. 3,702,886 and Re. No. 29,949, 3,709,979, 3,832,449,
35 4,556,447, 4,076,842, 4,016,245, 4,397,827, 4,650,655, 3,308,069, Re. 28,341 and EP 127,399. These zeolites may



be produced with differing silica:alumina ratios ranging from 12:1 upwards. Preferred molecular sieves include ZSM-5, ZSM-11, ZSM-12, ZSM-35 and MCM-22. Particularly preferred is ZSM-5.

5 In the invention, the catalyst preferably has a silica-alumina ratio less than 100, preferably 20 - 80 and an alpha value greater than 100, for example 150 - 2000. Alpha Value is an indication of the catalytic cracking activity of the catalyst compared to a standard catalyst
10 and gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time.) It is based on the activity of an amorphous 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
15 3,354,078 and in The Journal of Catalysis, Vol. 4, pp. 522-529 (August 1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980).

In the synthesis of zeolites, a reaction mixture is prepared generally containing an oxide of silicon,
20 optionally an aluminum source, a templating agent which is normally an organic nitrogen containing compound, and an alkaline aqueous medium.

The silicon oxide can be supplied from known sources such as silicates, silica hydrosol, precipitated silica
25 hydrosol, precipitated silica, e.g. Hi-Sil, silica gel, silicic acid. The aluminum oxide may be provided as only an impurity in another reactant, e.g., the silica source.

The sources of organic nitrogen-containing cations, depending, of course, on the particular zeolite product to
30 result from crystallization from the reaction mixture, may be primary, secondary or tertiary amines or quaternary ammonium compounds. Non-limiting examples of quaternary ammonium compounds include salts of tetramethylammonium, tetraethylammonium, tetrapropylammonium,
35 tetrabutylammonium, diethylammonium, triethylammonium, dibenzylammonium, dibenzyltrimethylammonium,



dibenzyl-diethylammonium, benzyltrimethylammonium and chlorine. Non-limiting examples of amines useful herein include the compounds of trimethylamine, triethylamine, tripropylamine, ethylenediamine, propanediamine, butanediamine, pentanediamine, hexanediamine, methylamine, ethylamine, propylamine, butylamine, diamethylamine, diethylamine, dipropylamine, benzylamine, aniline, pyridine, piperidine and pyrrolidine.

The sources of alkali or alkaline earth metal oxide may be, for example, sodium, lithium, calcium, magnesium, cesium or potassium hydroxides, halides (e.g. chlorides, and bromides), sulfates, nitrates, acetates, silicates, aluminates, phosphates and salts of carboxylic acids.

After crystallization of the zeolite, the organic cations are generally removed by calcination or other methods known in the art, and alkali or alkaline earth metals are generally removed, often by intermediate formation of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form.

After crystallization, zeolite crystals to be used in commercial processes are generally formed into agglomerates for improved strength and resistance to attrition. Various methods are used to agglomerate zeolite crystals. These methods include, for example, extrusion into pellets or beads, spray-drying into fluidizable microspheres, or by hot pressing the zeolite crystals into agglomerates.

In the present invention a silicon-modified zeolite molecular sieve catalyst is prepared by mixing zeolite crystals with an organosilicon compound and optionally a binder material, and agglomerating the mixture, followed by calcination of the agglomerate. Calcination is conveniently effected in an oxygen-containing atmosphere, preferably air, at a rate of 0.2° to 5°C/minute to a temperature greater 300° C but below a temperature at which the crystallinity of the zeolite is adversely affected. Generally, such temperature will be below 600°C.



Preferably the temperature of calcination is within the approximate range of 350° to 550°C. The product is maintained at the calcination temperature usually for 1 to 24 hours.

5 Zeolite crystals may be introduced into the mixture in as-synthesized form, and the organic template and alkali or alkaline earth metal ions remaining in the zeolite structure from the crystallization reaction mixture may be removed by methods known in the art after the crystals are
10 agglomerated.

 The organosilicon compound is added to the mixture in an aqueous form, for example, as an emulsion which may be surfactant stabilized, as a solution, or as an aerosol. Useful surfactants include, for example, ethers of
15 polyoxyethylene-octylphenols.

 The organosilicon compounds include silanes such as alkylsilanes, arylsilanes, alkyarylsilanes, alkoxysilanes, aryloxysilanes, oxyethylenesilanes, alkyaryloxysilanes, siloxanes and polysiloxanes with alkyl and/or aryl and/or
20 glycol groups. Alkyl is intended to include 1 to 12 carbons. Aryl is intended to include 6 to 10 carbons. The organosilicon compounds also include the silicone compounds described below which may also be used in trim selectivation. Preferred are siloxanes such as phenyl-
25 methylpolysiloxane.

 For the shape selective hydrocarbon conversion process of this invention, the suitable molecular sieve may be agglomerated or extruded in combination with a support or binder material such as, for example, a porous inorganic
30 oxide support or a clay binder. While the preferred binder is silica, other non-limiting examples of such binder materials include alumina, zirconia, magnesia, thoria, titania, boria and combinations thereof, generally in the form of dried inorganic oxide gels or gelatinous
35 precipitates. Suitable clay materials include, by way of example, bentonite and kieselguhr. The relative proportion



of suitable crystalline molecular sieve to the total composition of catalyst and binder or support may be 30 to 90 percent by weight and is preferably about 50-80 percent by weight of the composition. The composition may be in
5 the form of an extrudate, beads, pellets (tablets) or fluidizable microspheres.

Shape Selective Conversion

Molecular sieves which are selectivation agglomerated in accordance with the invention are generally useful as
10 catalysts in shape selective hydrocarbon conversion processes including cracking reactions involving dewaxing of hydrocarbon feedstocks; isomerization of alkylaromatics; oligomerization of olefins to form gasoline, distillate, lube oils or chemicals; transalkylation of aromatics;
15 alkylation of aromatics; conversion of oxygenates to hydrocarbons, rearrangement of oxygenates, and conversion of light paraffins and olefins to aromatics.

In general, catalytic conversion conditions over a catalyst comprising the modified zeolite include a
20 temperature of 100°C to 760°C, a pressure of 10 to 20,000 kPa (0.1 atmosphere (bar) to 200 atmospheres), a weight hourly space velocity of 0.08 hr⁻¹ to 2000 hr⁻¹ and a hydrogen/organic, e.g. hydrocarbon compound of 0 to 100.

The catalyst of the invention is particularly intended
25 for use in the transalkylation or disproportionation of toluene to produce para-xylene and this process will now be described as a representative example of shape selective conversion over the present catalyst.

Toluene Disproportionation

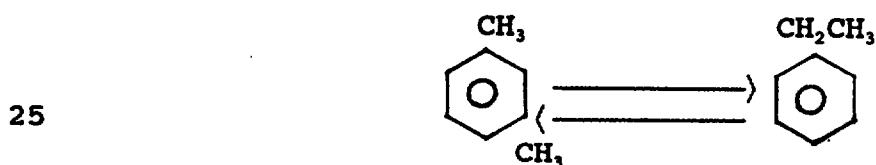
30 Reaction conditions in the toluene disproportionation contemplated herein include temperatures ranging from 350°C to 540°C, preferably greater than 400°C; pressures ranging from 100 to 34,500 kPa (0 to 5000 psig), preferably from 790 to 7000 kPa (100 to 1000 psig); a mole ratio of



hydrogen to hydrocarbons from 0.1 to 20, preferably from 2 to 4; at a weight hourly space velocity (WHSV) from 0.1 to 20 hr⁻¹, preferably from 2 to 4 hr⁻¹.

5 The toluene feedstock preferably includes 50% to 100% toluene, more preferably at least about 80% toluene in the toluene feedstock. Other compounds such as benzene, xylenes, and trimethylbenzene may also be present in the toluene feedstock without adversely affecting the present invention. The toluene feedstock may also be dried, if
10 desired, in a manner which will minimize moisture entering the reaction zone. Methods known in the art suitable for drying the toluene charge for the present process are numerous. These methods include percolation through any suitable desiccant, for example, silica gel, activated
15 alumina, molecular sieves or other suitable substances, or the use of liquid charge dryers.

Normally a single pass conversion of a toluene stream results in a product stream which includes dimethylbenzenes having alkyl groups at all locations, i.e., ortho-, meta-,
20 and para-xylenes. Furthermore, the xylenes are known to proceed in a reaction which produces unwanted ethylbenzenes (EB) by the following reaction:



Previously, the purity of p-xylene with respect to all of the C₈ products in a single pass has been limited to less than 90% when isomerization is permitted. This
30 efficiency is reduced somewhat by the production of ethylbenzene.

The present invention, however, provides high efficiency conversion which reduces production of ortho- and meta-isomers to the benefit of the desired para-isomer.
35 The resulting product stream contains greater than a 90%



purity of para-xylene. For example, the ortho-xylene isomer can be reduced to not more than about 0.5% of the total xylenes content while the meta-xylene isomer can be reduced to less than about 5% of the total xylene content.

5 Moreover, when the reaction system is properly treated, such as by deposition of platinum on the molecular sieve, the presence of ethylbenzene can be reduced to less than about 0.3% of the C₈ product.

10 As explained in greater detail herein, the present invention provides a method for obtaining para-xylene at conversion rates of at least about 15%, preferably at least about 20-25%, and with para-xylene purity of greater than 90%, preferably at least 95%, and most preferably about 99%.

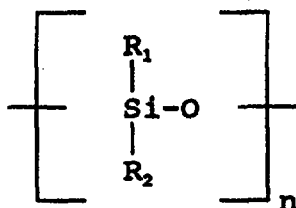
15 Therefore higher para-xylene purity can be attained at commercially acceptable conversion rates than with previously disclosed processes. The present invention thus allows for a significant reduction in process costs previously associated with the separation of unwanted by-
20 products. Toluene disproportionation processes of the prior art typically require expensive secondary and tertiary treatment procedures in order to obtain these efficiencies.

25 Preferably, the toluene disproportionation process of the present invention includes the step of effecting a further in-situ selectivation of the zeolite catalyst, in addition to the ex-situ preselectivation during catalyst agglomeration. This further in-situ selectivation, which is referred to herein as "trim selectivation", involves
30 contacting the catalyst simultaneously with toluene, a selectivating agent and hydrogen at reaction conditions until the desired p-xylene selectivity, e.g., 90% or 95%, is attained, whereupon the feed of selectivating agent is discontinued. The trim selectivating is preferably a
35 silicon-containing compound and more preferably a silicone-containing compound obeying the general formula:

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where R_1 is hydrogen, fluorine, hydroxy, alkyl, aryl,
 10 alkylaryl or fluoro-alkyl. The hydrocarbon substituents
 generally contain from 1 to 10 carbon atoms and preferably
 are methyl or ethyl groups. R_2 is selected from the same
 group as R_1 , and n is an integer of at least 2 and
 generally in the range of 3 to 1000. The molecular weight
 15 of the silicone compound employed is generally between 80
 and 20,000 and preferably between 150 and 10,000.
 Representative silicone compounds include dimethylsilicone,
 diethylsilicone, phenylmethylsilicone, methylhydrogensili-
 cone, ethylhydrogensilicone, phenylhydrogensilicone,
 20 methylethylsilicone, phenylethylsilicone, diphenylsilicone,
 methyltrifluoropropylsilicone, ethyltrifluoropropylsilicone,
 polydimethylsilicone, tetrachlorophenylmethyl silicone,
 tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen
 silicone, tetrachlorophenylphenyl silicone, methylvinyl-
 25 silicone and ethylvinylsilicone. The silicone compound
 need not be linear but may be cyclic as for example
 hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane,
 hexaphenylcyclotrisiloxane and octaphenylcyclotetra-
 siloxane. Mixtures of these compounds may also be used as
 30 well as silicones with other functional groups. Other
 silicon-containing compounds, such as silanes and
 siloxanes, may also be utilized.

Preferably, the kinetic diameters of the p-xylene trim
 selectivating agent and the silicon pre-selectivating
 35 compound added during zeolite agglomeration are larger than
 the zeolite pore diameter, in order to avoid reducing the
 internal activity of the catalyst.

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Reaction conditions for the trim-selectivation step generally include a temperature of 350° - 540°C and a pressure of about 100 to 34500 kPa (atmospheric - 5000 psig). The feed is provided to the system at a rate of about 0.1 - 20 WHSV. The hydrogen is fed at a hydrogen to hydrocarbon molar ratio of about 0.1-20. The trim-selectivating agent is preferably fed in an amount of 0.1% - 50% of the toluene and, depending upon the percentage of selectivating agent used, the trim selectivation will preferably last for 50-300 hours, most preferably less than 170 hrs.

While not wishing to be bound by theory, it is believed that the advantages of the present invention are obtained by rendering acid sites on the external surfaces of the catalyst substantially inaccessible to reactants while increasing catalyst tortuosity. Acid sites existing on the external surface of the catalyst are believed to isomerize the para-xylene exiting the catalyst pores back to an equilibrium level with the other two isomers thereby reducing the amount of para-xylene in the xylenes to only about 24%. By reducing the availability of these acid sites to the para-xylene exiting the pores of the catalyst, a relatively high level of para-xylene can be maintained. It is believed that the trim selectivating agents of the present invention block or otherwise render these external acid sites unavailable to the para-xylene by chemically modifying said sites.

The catalyst may be further modified in order to reduce the amount of undesirable by-products, particularly ethylbenzene. The state of the art is such that the reactor effluent from standard toluene disproportionation typically contains 0.5% ethylbenzene by-product. Upon distillation of the reaction products, the level of ethylbenzene in the C₈ fraction often increases to 3-4 percent. This level of ethylbenzene is unacceptable for polymer grade p-xylene since ethylbenzene in the C₈ product, if not



removed, degrades the quality of fibers ultimately produced from the p-xylene product. Consequently, ethylbenzene content must be kept low. The specification for ethylbenzene in the C₈ product has been determined by industry to be less than 0.3%. Ethylbenzene can be substantially removed by isomerization or by superfractionation processes. Removal of the ethylbenzene by conventional isomerization would be impractical with the present invention since the xylene stream, which includes greater than 90% para-xylene, would be concurrently isomerized to equilibrium xylenes reducing the amount of para-xylene in this xylene stream to about 24%. It is known in the art that the alternative procedure of removing the ethylbenzene by superfractionation is extremely expensive.

In order to avoid the need for downstream ethylbenzene removal, the level of ethylbenzene by-product is advantageously reduced by incorporating a hydrogenation-dehydrogenation function in the catalyst, such as by addition of a metal compound such as platinum. While platinum is the preferred metal, other metals such as palladium, nickel, copper, cobalt, molybdenum, rhodium, ruthenium, silver, gold, mercury, osmium, iron, zinc, cadmium, and mixtures thereof may be utilized. The metal may be added by cation exchange, in amounts of about 0.01 - 2%, typically about 0.5%. The metal must be able to enter the pores of the catalyst in order to survive a subsequent calcination step. For example, a platinum modified catalyst can be prepared by first adding the catalyst to a solution of ammonium nitrate in order to convert the catalyst to the ammonium form. The catalyst is subsequently contacted with an aqueous solution of tetraamine platinum(II) nitrate or tetraamine platinum(II) chloride. The metallic compound advantageously enters the pores of the catalyst. The catalyst can then be filtered, washed with water and calcined at temperatures of about 250° to 500°C.

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The effluent is separated and distilled to remove the desired product, i.e., para-xylene, plus other by-products.

By the present process, toluene can be converted to aromatic concentrates of high value, e.g., about 99% para-xylene based on all C₈ products. In a typical embodiment of the present process, optimum toluene conversion is found to be 20 - 25 weight percent with a para-xylene purity of 90 - 99%.

The following non-limiting examples illustrate the invention:

EXAMPLE 1

To 15.57g distilled water in a 150 cc beaker was added 1.01g 50% sodium hydroxide solution and 2.20g dimethyl silicon modified with oxyethylene groups to render it water soluble to 38C°. To this solution was added a mixture of 10.85g as-synthesized ZSM-5 and 5.85g hydrated amorphous silica with stirring. The resultant dry paste was extruded using a hand extruder to give well-formed 1.6mm (1/16) inch extrudate. Drying at 120°C for two hours gave 12.91g product.

EXAMPLE 2

To 15.58g distilled water in a 150cc beaker was added 1.03g 50% sodium hydroxide solution and a mixture of 4.06g phenylmethylpolysiloxane and 0.79g iso-Octylphenoxy-polyethoxyethanol surfactant to form an emulsion. To this emulsion was added a mixture of 10.85g as-synthesized ZSM-5 and 5.85g hydrated amorphous silica (HiSil, PPG Industries, Inc.) with stirring. The resultant dry paste was extruded using a hand extruder to give well-formed 1.6mm (1/16 inch) extrudate. Drying at 120°C for two hours gave 13.49g product.

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**CLAIMS:**

1. A catalyst comprising a crystalline molecular sieve having a Constraint Index of 1-12 which has been preselectivated by agglomerating a mixture comprising
5 then crystalline molecular sieve and an organosilicon compound and then calcining the resultant agglomerate.
2. A catalyst as claimed in claim 1, wherein the organosilicon compound is selected from silicones,
10 silanes, alkoxysilanes, siloxanes and polysiloxanes.
3. A catalyst as claimed in claim 1 or claim 2, and also including a hydrogenation/dehydrogenation metal.
4. A method for pre-selectivating a catalytic molecular sieve comprising forming a mixture comprising a
15 crystalline molecular sieve material having a Constraint Index of 1 to 12 and an organosilicon compound at a molecular sieve/organosilicon compound weight ratio of 1/10 to 100/1 and agglomerating the mixture.
- 20 5. A method as claimed in claim 30 further comprising contacting a pre-selectivated catalytic molecular sieve with a mixture comprising toluene and a second silicon source which is a paraxylene selectivating agent at reaction conditions for converting toluene to
25 xylene for a least one hour to yield a twice modified catalyst.



6. A process for shape selective hydrocarbon conversion comprising contacting the hydrocarbon with a catalyst comprising a crystalline molecular sieve having a Constraint Index of 1-12 which has been
5 preselectivated by agglomerating a mixture comprising then crystalline molecular sieve and an organosilicon compound and then calcining the resultant agglomerate.
7. A process as claimed in claim 5 wherein the shape
10 selective hydrocarbon conversion is selective disproportionation of toluene into para-xylene.
8. A process as claimed in claim 6 wherein the
15 disproportionation is effected at a temperature of 350°C to 540°C, a pressure of 100 to 34500 kPa (atmospheric to 5000 psig), a WHSV of 0.1 to 20, and a hydrogen to hydrocarbon molar ratio of 0.1 to 20.

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