

SELECTIVE PRODUCTION OF PARA-DIALKYL SUBSTITUTED BENZENES

This invention relates to a process for selective production of para-dialkyl substituted benzenes.

A representative para-dialkyl-substituted benzene is para-xylene. The production of para-xylene is typically performed by methylation of toluene or by toluene disproportionation over a catalyst under conversion conditions. Examples include the reaction of toluene with methanol as described by Chen et al., J. Amer. Chem. Soc. 101, 6783 (1979), and toluene disproportionation, as described by Pines in The Chemistry of Catalytic Hydrocarbon Conversions, 72, Academic Press, NY (1981). Such methods typically result in the production of a mixture of xylene isomers and, depending upon the degree of selectivity of the catalyst for para-xylene (para-selectivity) and the reaction conditions, different percentages of para-xylene are obtained.

Of the xylene isomers, i.e., ortho-, meta-, and para-xylene, meta-xylene is the least desired product and para-xylene is the most desired product. Para-xylene is of particular value being useful in the manufacture of terephthalic acid which is an intermediate in the manufacture of synthetic fibers, such as "Dacron". Mixtures of xylene isomers, whether alone or in further admixture with ethylbenzene, generally containing a concentration of about 24 wt.% para-xylene in the equilibrium mixture, have previously been separated by superfractionation and multistage refrigeration steps. Such processes not only involve high operation costs but offer limited yield.

Current commercial processes for the production of para-dialkyl substituted benzenes, such as, for example, para-xylene, employ zeolite catalysts, such as ZSM-5. One such process is disclosed in U.S. Patent No. 4,052,476 which relates to the disproportionation of toluene over a constraint index 1-12 zeolite, such as ZSM-5.

Various methods are known in the art for increasing the para-selectivity of zeolite catalysts. One such method is to modify the catalyst by treatment with a

"selectivating agent". For example, U.S. Patent Nos.

5 5,173,461; 4,950,835; 4,927,979; 4,477,583; 4,283,306; and 4,060,568 disclose specific methods for contacting a catalyst with a selectivating agent containing silicon.

U.S. Patent No. 4,548,914 describes another modification method involving impregnating catalysts with
10 oxides that are difficult to reduce, such as those of magnesium, calcium, and/or phosphorus, followed by treatment with water vapor to improve para-selectivity.

European Patent No. 296,582 describes the modification of aluminosilicate catalysts by impregnating such catalysts
15 with phosphorus-containing compounds and further modifying these catalysts by incorporating metals such as manganese, cobalt, silicon and Group IIA elements. The patent also describes the modification of zeolites with silicon containing compounds.

20 U.S. Patent No. 4,097,543 teaches a process for selective toluene disproportionation to yield increased para-xylene utilizing a specific crystalline zeolite catalyst, e.g., ZSM-5, which has undergone prior treatment to deposit a controlled amount of carbon coke thereon.

25 U.S. Patent No. 3,965,210 describes alkylation of toluene with methanol in the presence of a crystalline aluminosilicate zeolite, such as ZSM-5, which has been modified by contact with a polymer made up of meta-carborane units connected by siloxane units to selectively
30 yield para-xylene. These latter catalysts have, however, suffered from the serious deficiency of loss of selectivity upon air regeneration. This is attributable to breakage of carbon-silicon bonds upon exposure to the high temperature of regeneration giving rise to isolated clusters of silica
35 on the zeolite surface rather than the extensive surface coverage afforded by the technique described herein.

U.S. Patent Nos. 4,029,716 and 4,067,920 teach use of a specific catalyst, e.g., ZSM-5 or ZSM-11, which has been pretreated with a particular boron compound to produce para-xylene by alkylating toluene with an olefin.

5 U.S. Patent No. 4,117,026 teaches selective production of para-dialkyl substituted benzenes over catalyst comprising a large crystal zeolite, e.g., ZSM-5, having certain sorption characteristics.

10 U.S. Patent No. 4,465,886 teaches selective conversion of hydrocarbon compounds to product rich in para-dialkyl substituted benzenes over catalyst comprising a zeolite, e.g., ZSM-5, ZSM-5/ZSM-11 intermediate, ZSM-11, ZSM-12, ZSM-23, ZSM-35, or ZSM-48, having deposited thereon a coating of silica which covers exclusively the external
15 surface of the zeolite.

EP-A-457853 discloses toluene disproportionation of a feedstock containing C₉+ aromatics over zeolites MCM-22 and PSH-3.

20 The present invention resides in a process for the selective production of a para-dialkyl substituted benzene which comprises converting a feedstock comprising

(1) a mono-alkyl substituted benzene having an alkyl group of 1 to 4 carbon atoms, or

25 (2) a mixture of a mono-alkyl substituted benzene or benzene with an alkylating agent containing from 1 to 4 carbon atoms, to a product comprising a para-dialkyl substituted benzene containing alkyl groups of 1 to 4 carbon atoms by contact with a catalyst comprising a porous crystalline material characterized
30 by an X-ray diffraction pattern including the following lines:

	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	12.36 ± 0.4	m-vs
	11.03 ± 0.2	m-s
	8.83 ± 0.14	m-vs
5	6.18 ± 0.12	m-vs
	6.00 ± 0.10	w-m
	4.06 ± 0.07	w-s
	3.91 ± 0.07	m-vs
	3.42 ± 0.06	vs

- 10 said crystalline material having been treated with a selectivating agent and the treated crystalline material having an Alpha Value of 10 to 2000 and a p-xylene sorption capacity greater than 1 gram/100 grams of crystalline material, said sorption capacity being measured at 120°C
- 15 and a p-xylene pressure of 4.5 ± 0.8 mm of mercury (600 ± 100 kPa).

Typical examples of the process of the invention are the disproportionation of toluene and the alkylation of benzene or toluene with an alkylating agent, e.g.,

20 methanol.

The catalyst employed in the process of the invention comprises a synthetic porous crystalline material which, in its calcined form, is characterized by an X-ray diffraction pattern including the following lines:

25

TABLE A

	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	12.36 ± 0.4	m-vs
	11.03 ± 0.2	m-s
	8.83 ± 0.14	m-vs
30	6.18 ± 0.12	m-vs
	6.00 ± 0.10	w-m
	4.06 ± 0.07	w-s
	3.91 ± 0.07	m-vs
	3.42 ± 0.06	vs

Alternatively, the synthetic porous crystalline material employed in the process of the invention may be characterized by an X-ray diffraction pattern in its calcined form including the following lines:

5	<u>TABLE B</u>	
	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	30.0 ± 2.2	w-m
	22.1 ± 1.3	w
	12.36 ± 0.4	m-vs
10	11.03 ± 0.2	m-s
	8.83 ± 0.14	m-vs
	6.18 ± 0.12	m-vs
	6.00 ± 0.10	w-m
	4.06 ± 0.07	w-s
15	3.91 ± 0.07	m-vs
	3.42 ± 0.06	vs

More specifically, the calcined form of the synthetic porous crystalline material employed in the process of the invention may be characterized by an X-ray diffraction pattern including the following lines:

20

TABLE C

	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	12.36 ± 0.4	m-vs
	11.03 ± 0.2	m-s
5	8.83 ± 0.14	m-vs
	6.86 ± 0.14	w-m
	6.18 ± 0.12	m-vs
	6.00 ± 0.10	w-m
	5.54 ± 0.10	w-m
10	4.92 ± 0.09	w
	4.64 ± 0.08	w
	4.41 ± 0.08	w-m
	4.25 ± 0.08	w
	4.10 ± 0.07	w-s
15	4.06 ± 0.07	w-s
	3.91 ± 0.07	m-vs
	3.75 ± 0.06	w-m
	3.56 ± 0.06	w-m
	3.42 ± 0.06	vs
20	3.30 ± 0.05	w-m
	3.20 ± 0.05	w-m
	3.14 ± 0.05	w-m
	3.07 ± 0.05	w
	2.99 ± 0.05	w
25	2.82 ± 0.05	w
	2.78 ± 0.05	w
	2.68 ± 0.05	w
	2.59 ± 0.05	w

Most specifically, the calcined form of the synthetic
 30 porous crystalline material employed in the process of the
 invention may be characterized in its calcined form by an
 X-ray diffraction pattern including the following lines:

TABLE D

	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	30.0 ± 2.2	w-m
	22.1 ± 1.3	w
5	12.36 ± 0.4	m-vs
	11.03 ± 0.2	m-s
	8.83 ± 0.14	m-vs
	6.86 ± 0.14	w-m
	6.18 ± 0.12	m-vs
10	6.00 ± 0.10	w-m
	5.54 ± 0.10	w-m
	4.92 ± 0.09	w
	4.64 ± 0.08	w
	4.41 ± 0.08	w-m
15	4.25 ± 0.08	w
	4.10 ± 0.07	w-s
	4.06 ± 0.07	w-s
	3.91 ± 0.07	m-vs
	3.75 ± 0.06	w-m
20	3.56 ± 0.06	w-m
	3.42 ± 0.06	vs
	3.30 ± 0.05	w-m
	3.20 ± 0.05	w-m
	3.14 ± 0.05	w-m
25	3.07 ± 0.05	w
	2.99 ± 0.05	w
	2.82 ± 0.05	w
	2.78 ± 0.05	w
	2.68 ± 0.05	w
30	2.59 ± 0.05	w

Examples of the above porous crystalline materials include the zeolites PSH-3 described in U.S. Patent No. 4,439,409, MCM-22 described in U.S. Patent No. 4,954,325 and MCM-49 described in U.S. Patent No. 5,236,575. These materials have partial, large-pore structure

characteristics and exhibit an unusual amount of external acid activity, possibly due to the presence of large, 12-membered ring exterior pockets which do not connect with the internal pore system. The internal pore structures of this class of crystals are believed to consist of two-dimensional, 10-membered ring systems which intersect to access large supercages. The total catalytic activity of these materials is, therefore, believed to be a composite of 10-membered ring, 12-membered ring pocket, and supercage activity. These large-pore characteristics suggest that effecting shape selectivity in these materials would be difficult. However, modification of these materials with molecular or polymeric species whose molecular diameters are chosen to selectively alter access to one or more of these catalytically active sites produces novel catalytic behavior, as exemplified below.

It may be desired to incorporate the crystalline material with another material which is resistant to the temperatures and other conditions employed in the condensation process of this invention. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clay, silica, and/or metal oxides such as alumina, magnesia, zirconia, thoria, beryllia, and/or titania. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the zeolite, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion so that the products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush

strength of the catalyst under commercial operating conditions. Said materials, i.e., clays oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

Naturally occurring clays which can be composited with zeolite crystals include the montmorillonite and kaolin families which include the subbentonites 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. Binders useful for compositing with the zeolite also include inorganic oxides, notably alumina.

In addition to the foregoing materials, the crystals can be composited with a porous matrix material such as 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. It may also be advantageous to provide at least a part of the foregoing matrix materials in colloidal form to facilitate extrusion of the bound catalyst components.

The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

Prior to its use as catalyst in the present process, the crystalline material should be subjected to thermal treatment to remove part or all of any organic constituent

present therein. This thermal treatment is generally performed by heating at a temperature of at least 370°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is preferred simply for reasons of convenience. The thermal treatment can be performed at a temperature of up to 925°C.

The porous crystalline material used in the process of the invention is treated with a selectivating described in detail below. The treated crystalline material has an activity, in terms of Alpha Value, of 10 to 2000, preferably 100 to 600; and (iii) a para-xylene sorption capacity greater than 1 gram/100 grams of crystalline material, preferably from 5 to 10 grams/100 grams of crystalline material, the sorption capacity measured at 120°C and a p-xylene pressure of 4.5 ± 0.8 mm of mercury.

When Alpha Value is examined, it is noted that the Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst 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 silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant = 0.016 sec^{-1}). The Alpha Test is described in U.S. Patent 3,354,078; in the Journal of Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980). The experimental conditions of the test used herein include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, 61, 395.

The measurement of p-xylene sorption capacity is conveniently carried out gravimetrically in a thermal balance. In particular, it has been found that an equilibrium sorption capacity of p-xylene of at least 1 gram/100 grams of zeolite, preferably from 5 to 10 grams/100 grams of zeolite, measured at 120°C and a p-xylene pressure of 4.5 ± 0.8 mm of mercury (600 ± 100 kPa)

This Sheet Has Been Replaced

-11-

is required in order to achieve the desired selective production of para-dialkyl substituted benzenes in this process.

As previously stated, the crystalline material for use herein must be treated with a selectivating agent which alters the diffusion properties of the crystal. Suitable selectivating agents include, for example, silicon-containing compounds such as monomeric or polymeric siloxanes, other main group species (e.g., those containing Ge, B, P, Mg, and/or Sb) which decompose to oxide or non-oxide ceramics, or solid-state carbon species.

Useful selectivating agents include siloxanes which can be characterized by the general formula:



where R_1 is hydrogen; halogen; hydroxyl; alkyl or halogenated alkyl of from 1 to 10 carbons; or aryl, halogenated aryl, aralkyl, halogenated aralkyl, alkaryl or halogenated alkaryl of from 6 to 20 carbons. The hydrocarbon substituents generally contain from 1 to 10 carbon atoms, preferably methyl or ethyl groups. R_2 is independently 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 of the silicone compound employed is generally between 80 and 20,000 and preferably within the range of 150 to 10,000. Representative silicone compounds include dimethyl silicone, diethyl silicone, phenylmethyl silicone, methylhydrogen silicone, ethylhydrogen silicone, phenylhydrogen silicone, methyl-ethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachlorophenylmethyl

This Sheet Has Been Replaced

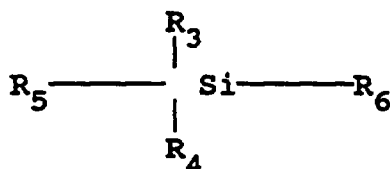
-12-



silicone, ~~tetrachlorophenylethyl~~ silicone, tetra-
chlorophenylhydrogen silicone, tetrachlorophenylphenyl
silicone, methylvinyl silicone and ethylvinyl silicone.

The silicone compound need not be linear, but may be
cyclic, for example, hexamethyl cyclotrisiloxane,
octamethyl cyclotetrasiloxane, hexaphenyl cyclotrisiloxane
and octaphenyl cyclotetrasiloxane. Mixtures of these
compounds may also be used, as may silicones with other
functional groups.

Other, more preferred silicon compounds, including
silanes, alkoxy silanes, and organoamine silanes, may also
be utilized. These useful silicon-containing selectivating
agents include silanes characterizable by the general
formula:



where R_3 , R_4 , R_5 and R_6 are independently selected from the
group consisting of hydrogen; hydroxyl; halogen; alkyl of
from 1 to 10 carbons; halogenated alkyl of from 1 to 10
carbons; alkoxy; aryl, halogenated aryl, aralkyl,
halogenated aralkyl, alkaryl, or halogenated alkaryl of
from 6 to 20 carbons; and organoamine groups of from 3 to 9
carbons. Most preferably R_3 , R_4 , R_5 and R_6 are
independently selected from the group consisting of -
 $N(CH_3)_3$, $-N(C_2H_5)_3$ and $-N(C_3H_7)_3$. Mixtures of these
compounds may also be used.

Such compounds are preferred because of their
amphiphilic character, allowing their dissolution, or at
least emulsification, in aqueous carriers, as well as
taking advantage of the hydrophobic character of the
zeolite on which the silicon compounds are being deposited.

The kinetic diameter of the selectivating agent is
preferably larger than the zeolite pore diameter, in order

to avoid entry of the selectivating agent into the pore and any concomitant reduction in the internal activity of the catalyst. When a silicon compound is used that is of a size small enough to enter the pores of the catalyst
5 crystal, it is desirable to use the sodium form of the zeolite rather than the hydrogen form.

For use in the present invention, the zeolite, either incorporated with a binder or in unbound form, is impregnated with the selectivating agent. Selectivation can
10 be effected in situ in the reactor used to effect the process of the invention or ex situ prior to introduction of the catalyst into the reactor.

In situ selectivation is conveniently effected by introducing a source of the selectivating agent into the reactor with the aromatic feed, such as toluene, for at
15 least an initial selectivation period of the process.

Ex situ selectivation is effected by depositing the selectivating agent on the external surface of the catalyst by any suitable method. Conveniently, the deposition is
20 repeated a number of times, preferably 2 to 6 times, to produce multiple coatings of the selectivating agent on the catalyst. For example, the selectivating agent may be dissolved in a carrier, mixed with the catalyst and then dried by evaporation or vacuum distillation. This method
25 is termed "impregnation". The molecular sieve may be contacted with the silicon compound at a molecular sieve/silicon compound weight ratio of 100/1 to 1/100.

The silicon compound employed may be in the form of a solution, an emulsion, a liquid or a gas under the
30 conditions of contact with the zeolite. Not wishing to be bound by theory, it is believed that the deposited silicon compound extensively covers, and resides substantially exclusively on, the external surface of the molecular sieve. Examples of methods of depositing silicon on the
35 surface of a zeolite are found in U.S. Patent Nos. 4,090,981; 4,127,616; 4,465,886; and 4,477,583. Further

examples of silicon deposition on zeolite surfaces are described in Nakajima, H. et al., Sekiyu Gakkaishi, 35(2) (1992), and U.S. Patent No. 4,950,835 to Wang et al.

Following each deposition of the silicon compound, the catalyst is calcined to decompose the molecular or polymeric species to a solid state species. The catalyst may be calcined at a rate of 0.2°C/minute to 5°C/minute to a temperature greater than 200°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°C to 550°C. The product is maintained at the calcination temperature usually for 1 to 24 hours, preferably for between 2 and 6 hours.

The catalyst may be calcined in an atmosphere of N₂, an oxygen-containing atmosphere, preferably air, an atmosphere of N₂ followed by an oxygen-containing atmosphere, or an atmosphere containing a mixture of N₂ and air. Calcination should be performed in an atmosphere substantially free of water vapor, to avoid undesirable uncontrolled steaming of the silicon coated catalyst. The catalyst may be calcined once or more than once after each silicon deposition. The various calcinations in any impregnation sequence need not be identical, but may vary with respect to the temperature, the rate of temperature rise, the atmosphere and the duration of calcination.

Factors upon which the amount of silica incorporated with the zeolite is dependent include temperature, concentration of the silicon compound in the containing medium, the degree to which the zeolite has been dried prior to contact with the silicon compound, and calcination of the zeolite.

After the selectivation sequence, the catalyst is preferably exchanged at least once with NH₄⁺ ions by immersing the catalyst in a solution containing NH₄⁺ ions. Most preferably the concentration of NH₄⁺ ions is

approximately 1M. The NH_4^+ solution may include various inorganic anions, most preferably NO_3^- . Most preferably, the NH_4^+ exchange is performed three times.

After the NH_4^+ exchange sequence, if any, the catalyst
5 may be subjected to steam treatment with 1% to 100% steam, preferably 50% to 100% steam, at a temperature of 100°C to 600°C, preferably 175°C to 325°C and a pressure of 0.01 to 50 psia (0.07 to 345 kPa) for 2 to 12 hours, preferably 3 to 6 hours. Such controlled steaming may further improve
10 the selectivity of the catalyst.

The modified zeolite catalysts for use in the invention facilitate the conversion of alkylbenzene compounds to provide dialkyl-substituted benzene products containing alkyl groups of 1 to 4 carbon atoms, such as
15 xylene, which are highly enriched in the para-dialkyl-substituted benzene isomer. Conversion reactions of this type include aromatics alkylation, transalkylation and disproportionation.

In general, catalytic conversion conditions over the
20 modified catalyst of the invention include a temperature of 100°C to 760°C, a pressure of 0.1 to 200 atmospheres (10 to 20,000 kPa), a weight hourly space velocity of 0.08 to 2000 hr^{-1} , and a hydrogen/organic, e.g., hydrocarbon, compound mole ratio of 0 (no added hydrogen) to 100.

The present invention is described in detail below in
25 relation to its preferred application in the disproportionation of alkyl-substituted benzenes, particularly toluene. In this application, the preferred process conditions include a reactor inlet temperature of
30 200°C to 600°C, preferably 350°C to 500°C; a pressure of 100 to 35000 kPa (atmospheric to 5000 psig), preferably 800 to 7000 kPa (100 to 1000 psig); a WHSV of 0.1 to 20 hr^{-1} , preferably 2 to 10 hr^{-1} ; and a H_2/HC mole ratio of 0.05 to 20, preferably 0.1 to 6.

35 Where the catalyst is employed in the disproportionation of toluene, the level of ethylbenzene by-product is

advantageously reduced by incorporating a hydrogenation/dehydrogenation function within the catalyst, such as by addition of a metal compound such as platinum. While platinum is the preferred metal, other metals of Groups IB to VIII of the Periodic Table 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 an amount of 0.01% to 2%, typically about 0.5%, by weight. It is desirable that the metal be able to enter the pores of the catalyst. 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 a temperature of 250°C to 500°C.

The invention will now be more particularly described with reference to the following examples.

Toluene disproportionation experiments were conducted in an automated unit with on-line sampling. In these experiments, approximately 1 gram of catalyst (0.125 inch [0.3 cm] extrudate) was loaded into a 0.25 inch (0.6 cm) diameter stainless steel tube reactor. The catalyst was heated to 538°C in 200 cc/minute air at a heating rate of 2°C/minute in each instance.

Example 1

A sample of MCM-49 in the hydrogen form, i.e., HMCM-49, having a crystal size of 0.1-0.5 micron, an Alpha Value of about 450, and a p-xylene sorption capacity of about 10 grams/ 100 grams was mixed with alumina binder to provide a catalyst comprising 65 wt.% HMCM-49 and 35 wt.% alumina.

The mixture was used to prepare 1/16 inch (0.16 cm) extrudate catalyst for use in the present process.

Example 2

5 A sample of MCM-22 in the hydrogen form, i.e., HMCM-22, having a crystal size of 0.1-0.5 micron, an Alpha Value of about 450, and a p-xylene sorption capacity of about 10 grams/ 100 grams was mixed with alumina binder to provide a catalyst comprising 65 wt.% HMCM-22 and 35 wt.% alumina. The mixture was used to prepare 1/16 inch (0.16 cm)
10 extrudate catalyst for use in the present process.

Example 3

A sample of MCM-22 in the hydrogen form, i.e., HMCM-22, having a crystal size of 0.1-0.5 micron, an Alpha Value of about 450, and a p-xylene sorption capacity of about 10
15 grams/ 100 grams was mixed with silica binder to provide a catalyst comprising 65 wt.% HMCM-22 and 35 wt.% silica. The mixture was used to prepare 1/16 inch (0.16 cm) extrudate catalyst for use in the present process.

Example 4

20 This toluene disproportionation experiment involved the catalyst prepared in Example 1. Following the heating activation step described above, the experiment was initiated with pure toluene feed at 424°C, 4 hr⁻¹ WHSV, 2 H₂/HC mole ratio, and 3550 kPa (500 psig). As shown in
25 Table G, the catalyst was active and produced 24% para-xylene product at 20% conversion. A temperature scan showed that the catalyst produced near equilibrium para-xylene product under these conditions at all temperatures between 424°C and 505°C. A WHSV scan at 464°C also showed
30 near equilibrium para-xylene at conversions between 8 and 46%. At this point, a toluene feed containing 1.0 wt.% of dimethylphenylmethylpolysiloxane (Dow-550) was admitted to

the reactor at 485°C, 4 hr⁻¹ WHSV, 2 H₂/HC mole ratio, and 3550 kPa (500 psig).

5 An examination of the selectivity/conversion data (Table G) shows a rapid increase in selectivity over about 20 hours on stream. For example, after 7 hours of selectivation, the catalyst produced 56% para-xylene product at 7% conversion. This selectivity is far higher than an equilibrium distribution of xylene products and much more selective than the parent material at comparable
10 conversion. Thus, the treatment with the silicone compound increased the shape selectivity of the disproportionation reaction.

To determine the level of permanence of the selectivation, the catalyst was regenerated by heating in
15 air to 538°C at a rate of 2°C/minute. After regeneration, the initial sample taken at 485°C, 4 hr⁻¹ WHSV, 2 H₂/HC mole ratio, and 3550 kPa (500 psig) on pure toluene feed showed 26% para-xylene product at 15% conversion. Thus, the catalyst displayed a decrease in selectivity after the
20 regeneration; however, it still displayed enhanced selectivity compared to the parent catalyst material.

In Table G, samples 1-10 involved pure toluene feed, samples 11-16 involved the feed having DOW-550 added, and samples 18-19 involved pure toluene feed.

TABLE G (cont.)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
p-Xylene(X)	24.40	24.24	24.01	23.87	23.83	24.05	24.00	24.01	24.28	24.77
m-Xylene(X)	53.32	53.06	52.73	52.73	52.24	52.78	52.77	53.04	53.07	53.04
5 o-Xylene(X)	22.28	22.70	23.26	23.40	23.94	23.17	23.23	22.95	22.65	22.19
p-Xylene(E)	104.09	103.42	102.45	101.85	101.64	102.60	102.38	102.45	103.59	105.69
m-Xylene(E)	102.28	101.78	101.15	101.14	100.21	101.25	101.23	101.74	101.80	101.74
o-Xylene(E)	91.21	92.92	95.20	95.78	97.98	94.85	95.08	93.95	92.71	90.83
Toluene										
10 conv.	20.41	27.78	36.19	43.63	49.74	46.06	34.08	23.29	13.67	8.05
Benzene/ xylene(mol)	1.08	1.16	1.21	1.25	1.34	1.21	1.14	1.10	1.08	1.07

TABLE G (cont.)

Sample	11	12	13	14	15	16	17	18
Temp, °C	485.40	485.60	485.60	484.70	484.70	484.70	484.90	484.70
Pressure, psig	500.70	507.00	499.00	498.70	498.00	499.00	494.70	497.20
5 WHSV, hr ⁻¹	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
H ₂ /HC (mol)	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99
TOS, hours	36.92	39.63	43.70	47.75	51.82	55.88	61.32	64.03
C ₅ -	3.99	3.60	1.84	1.18	0.95	0.06	2.18	1.22
Benzene	18.57	6.54	2.29	2.04	1.99	1.93	6.20	9.40
10 Toluene	52.82	79.98	92.98	94.34	94.74	95.15	84.60	77.53
Ethylbenzene	0.58	0.14	0.00	0.00	0.00	0.00	0.15	0.18
p-Xylene	5.13	3.90	1.62	1.45	1.42	1.37	1.50	2.54
m-Xylene	11.20	4.53	1.14	0.92	0.85	0.83	3.01	5.47
o-Xylene	4.99	0.92	0.12	0.07	0.06	0.06	1.34	2.43
15 Ethyltoluene	0.67	0.29	0.00	0.00	0.00	0.00	0.74	0.63
Trimethylbenzene	1.86	0.10	2.62	2.11	0.00	0.00	0.29	0.60
Diethylbenzene	0.20	0.00	0.29	0.21	0.00	0.00	0.00	0.00
Dimethylethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetramethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20 Other	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p-Xylene (X)	24.05	41.73	56.26	59.44	60.86	60.71	25.62	24.31
m-Xylene (X)	52.54	48.46	39.67	37.63	36.72	36.65	51.42	52.40

TABLE G (cont.)

<u>Sample</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
o-Xylene (X)	23.41	9.81	4.07	2.93	2.42	2.64	22.96	23.29
p-Xylene (E)	102.62	178.02	240.03	253.58	259.65	258.99	109.32	103.72
m-Xylene (E)	100.79	92.97	76.10	72.19	70.43	70.30	98.63	100.52
o-Xylene (E)	95.81	40.15	16.64	11.99	9.91	10.82	93.98	95.32
Toluene conv.	47.18	20.02	7.01	5.66	5.26	4.85	15.40	22.47
Benzene/xylene (mol)	1.18	0.95	1.08	1.14	1.16	1.16	1.44	1.22

Example 5

In this experiment, the parent HMCM-22/ Al_2O_3 material of Example 2 was subjected to an impregnation/ calcination procedure with Dow-550 silicone as follows.

5 To 2.0 grams of the HMCM-22/ Al_2O_3 extrudate was added 0.3927 grams of Dow-550 dissolved in 20 grams of hexane. The catalyst was agitated in the silicone solution for several minutes and the hexane distilled off by high vacuum distillation. The dry catalyst was then calcined at
10 $1^\circ/\text{minute}$ in nitrogen to 538°C . After allowing the sample to cool to room temperature, the sample was then calcined in air at $1^\circ/\text{minute}$ to 538°C and held for 3 hours. The silica-modified catalyst had gained 6.46 wt.%, presumably as SiO_2 .

15 After catalyst activation as described above, the experiment was initiated with pure toluene feed at 424°C , 4 hr^{-1} WHSV, 2 H_2/HC mole ratio, and 3550 kPa (500 psig). As shown in Table H, the catalyst was active and produced 24% para-xylene product at 27% conversion. A temperature
20 scan showed that the catalyst produced near equilibrium para-xylene product under these conditions at all temperatures between 424°C and 505°C . At this point, a toluene feed containing 0.5 wt.% of dimethylphenyl-methylpolysiloxane (Dow-550) was admitted to the reactor at
25 485°C , 4 hr^{-1} WHSV, 2 H_2/HC mole ratio, and 3550 kPa (500 psig).

An examination of the selectivity/conversion data (Table H) shows a rapid increase in selectivity over about 13 hours on stream, at which point the catalyst produced
30 62% para-xylene product at 11% conversion. This selectivity, as indicated above, is far higher than an equilibrium distribution of xylene products and much more than that of the parent material at comparable conversion. Thus, the treatment with silicone has increased the shape
35 selectivity of the disproportionation reaction.

To determine the level of permanence of the selectivation, the catalyst was regenerated as in Example 4. After regeneration, the initial sample taken at 485°C, 4 hr⁻¹ WHSV, 2 H₂/HC mole ratio, and 3550 kPa (500 psig) on pure toluene feed showed 27% para-xylene at 14% conversion. Thus, the catalyst displayed a decrease in selectivity after the regeneration; however, it still displayed enhanced selectivity compared to the parent material.

In Table H, samples 1-5 involved pure toluene feed, samples 6-10 involved the feed having DOW-550 added, and samples 11-13 involved pure toluene feed.

TABLE H

Sample	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Temp, °C	425.40	445.20	465.30	484.90	504.70	484.90	484.90	484.90
Pressure, psig	497.70	497.50	498.00	499.70	501.50	503.20	502.70	503.00
5 WHSV, hr ⁻¹	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
H ₂ /HC (mol)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
TOS, hours	2.72	6.78	10.83	10.83	18.97	21.70	24.40	28.47
C ₅ -	0.59	0.88	1.24	1.62	2.11	3.55	4.35	2.99
Benzene	11.50	13.77	16.20	18.31	20.09	18.21	15.2	17.37
10 Toluene	73.03	66.94	61.65	56.65	53.75	54.87	58.22	78.25
Ethylbenzene	0.14	0.2	10.31	0.40	0.47	0.54	0.52	0.19
p-Xylene	3.36	4.05	4.50	4.95	5.21	4.92	4.94	4.96
m-Xylene	7.30	8.82	9.85	10.78	11.33	10.68	10.38	4.74
o-Xylene	3.09	3.82	4.30	4.81	5.03	4.75	4.45	1.07
15 Ethyltoluene	0.35	0.45	0.51	0.53	0.53	0.73	0.85	0.37
Trimethylbenzene	0.63	0.96	1.31	1.68	1.97	1.58	0.96	0.09
Diethylbenzene	0.00	0.10	0.13	0.17	0.21	0.16	0.10	0.00
Dimethylethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetramethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20 Other	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p-Xylene (X)	24.42	24.28	24.10	24.12	24.16	24.18	25.00	46.05

TABLE H (cont.)

Sample	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
m-Xylene (X)	53.08	52.85	52.83	52.46	52.53	52.49	52.51	44.02
o-Xylene (X)	22.50	22.87	23.07	23.42	23.31	23.33	22.49	9.94
p-Xylene (E)	104.18	103.59	102.83	102.89	103.08	103.18	106.66	196.44
m-Xylene (E)	101.82	101.38	101.33	100.63	100.77	100.68	100.72	84.44
o-Xylene (E)	92.12	93.61	94.44	95.88	95.40	95.49	92.08	40.67
Toluene conv.	26.97	33.06	38.35	43.25	46.95	45.13	41.78	21.75
Benzene/xylene (mol)	1.14	1.12	1.18	1.21	1.27	1.22	1.05	0.93

TABLE H (cont.)

		9	10	11	12	13
<u>Sample</u>						
5	Temp, °C	484.90	485.10	425.40	445.40	465.30
	Pressure, psig	502.70	504.20	498.00	497.20	502.70
	WHSV, hr ⁻¹	4.00	4.00	4.00	4.00	4.00
	H ₂ /HC (mol)	2.00	2.00	2.00	2.00	2.00
	TOS, hours	31.18	35.23	38.43	41.13	43.70
10	C ₅ -	3.32	2.49	0.49	0.79	0.79
	Benzene	5.16	3.71	5.89	7.84	7.84
	Toluene	84.90	89.00	86.21	81.64	81.64
	Ethylbenzene	0.00	0.00	0.00	0.97	0.07
	p-Xylene	3.75	2.91	1.90	2.37	2.37
15	m-Xylene	2.43	1.63	3.76	4.79	4.79
	o-Xylene	0.29	0.16	1.53	2.00	2.00
	Ethyltoluene	0.15	0.11	0.22	0.29	0.29
	Trimethylbenzene	0.00	0.00	0.08	0.22	0.22
	Diethylbenzene	0.00	0.00	0.00	0.00	0.00
20	Dimethylethylbenzene	0.00	0.00	0.00	0.00	0.00
	Tetramethylbenzene	0.00	0.00	0.00	0.00	0.00
	Other	0.00	0.00	0.00	0.00	0.00
	p-Xylene (X)	57.95	61.97	26.50	25.84	25.44
	m-Xylene (X)	37.55	34.72	52.27	52.30	22.21

TABLE H (cont.)

<u>Sample</u>	<u>2</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>
o-Xylene (X)	4.51	3.31	21.23	21.86	4.07
p-Xylene (E)	247.21	264.38	113.06	110.24	108.51
m-Xylene (E)	72.02	66.60	100.26	100.33	100.42
o-Xylene (E)	18.46	13.55	86.91	89.46	90.93
Toluene conv.	15.09	10.99	13.78	18.35	22.51
Benzene/xylene (mol)	1.08	1.08	1.11	1.16	51.21

Example 6

This toluene disproportionation experiment involved the catalyst prepared in Example 3. Following the heating activation step described above, the experiment was
5 initiated with pure toluene feed at 485°C, 4 hr⁻¹ WHSV, 2 H₂/HC mole ratio, and 3550 kPa (500 psig). As shown in Table I, the catalyst was active and produced 24% para-xylene product at 47% conversion.

After 19 hours on stream, a toluene feed containing
10 1.0 wt.% of dimethylphenylmethylpolysiloxane (Dow-500) was admitted to the reactor at 485°C, 4 hr⁻¹ WHSV, 2 H₂/HC, mole ratio, and 3550 kPa (500 psig).

An examination of the selectivity/conversion data (Table I) shows an increase in selectivity over about 22
15 hours on stream. For example, after 19 hours of selectivation, the catalyst produced 44% para-xylene product at 24% conversion. Thus, the treatment with the silicone compound increased the shape selectivity of the disproportionation reaction.

20 In Table I, samples 1-7 involved pure toluene feed and samples 8-13 involved the feed having DOW-550 added.

TABLE I

Sample	1	2	3	4	5	6	7
Temp, °C	485.40	485.10	485.40	485.40	485.10	485.10	485.10
Pressure, psig	503.70	498.30	497.70	505.00	498.30	500.70	501.50
WHSV, hr ⁻¹	3.99	3.99	3.99	3.99	3.99	3.99	3.99
H ₂ /HC (mol)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
TOS, hours	2.70	5.40	10.83	13.55	16.25	18.95	22.77
C ₅ -	2.29	1.96	1.47	1.43	1.49	1.47	2.98
Benzene	19.84	19.67	19.35	19.13	19.67	19.74	18.75
Toluene	53.32	53.58	54.16	54.09	53.78	53.78	52.63
Ethylbenzene	0.51	0.45	0.39	0.38	0.34	0.34	0.49
p-Xylene	5.12	5.21	5.30	5.40	5.34	5.34	5.52
m-Xylene	11.17	11.4	11.70	11.88	11.84	11.84	12.22
o-Xylene	5.00	5.11	5.21	5.31	5.24	5.27	5.40
Ethyltoluene	0.62	0.54	0.48	0.45	0.42	0.41	0.62
Trimethylbenzene	1.87	1.81	1.76	1.74	1.67	1.64	1.26
Diethylbenzene	0.23	0.21	0.19	0.18	0.17	0.17	0.12
Dimethylethylbenzene	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Tetramethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Other	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p-Xylene (X)	24.04	23.92	23.84	23.90	23.84	23.79	23.85

TABLE I (cont.)

Sample	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
m-Xylene (X)	52.47	52.62	52.70	52.58	52.76	52.74	52.81
o-Xylene (X)	23.50	23.46	23.46	23.52	23.40	23.47	23.34
p-Xylene (E)	102.54	102.05	101.72	101.95	101.51	101.51	101.75
Toluene conv.	46.68	46.42	45.84	45.91	46.16	46.22	47.37
Benzene/xylene (mol)	1.27	1.23	1.18	1.15	1.19	1.20	1.10

TABLE I (cont.)

Sample	8	9	10	11	12	13
Temp, °C	485.10	485.10	485.10	485.10	485.10	485.10
Pressure, psig	502.70	488.00	485.20	485.00	492.00	513.00
WHSV, hr ⁻¹	3.99	3.99	3.99	3.99	3.99	3.99
H ₂ /HC (mol)	2.00	2.00	2.00	2.00	2.00	2.00
TOS, hours	25.50	29.55	33.62	37.68	41.75	46.02
C ₅ -	3.32	3.18	12.75	2.55	2.29	12.92
Benzene	15.20	11.91	0.00	8.72	7.99	0.00
Toluene	58.86	67.41	72.85	76.66	78.56	71.27
Ethylbenzene	0.46	0.31	0.21	0.14	0.11	0.19
p-Xylene	5.69	5.92	5.60	5.03	4.70	3.46
m-Xylene	11.65	8.88	6.96	5.70	5.25	7.50
o-Xylene	3.74	1.80	1.20	0.87	0.75	3.36
Ethyltoluene	0.66	0.49	0.37	0.27	0.23	0.51
Trimethylbenzene	0.35	0.12	0.06	0.04	0.03	0.64
Diethylbenzene	0.05	0.00	0.00	0.00	0.00	0.00
Dimethyl-ethylbenzene	0.00	0.00	0.00	0.00	0.00	0.15
Tetramethylbenzene	0.00	0.00	0.00	0.00	0.00	0.00
Other	0.00	0.00	0.00	0.00	0.00	0.00
p-Xylene (X)	27.00	35.68	40.71	43.36	43.94	24.16

TABLE I (cont.)

Sample	<u>8</u>	<u>9</u>	<u>TABLE I (cont.)</u>			<u>12</u>	<u>13</u>
			<u>10</u>	<u>11</u>	<u>12</u>		
m-Xylene (X)	55.24	53.48	50.54	49.13	49.09	52.37	
o-Xylene (X)	17.65	10.84	8.75	7.51	6.97	23.47	
p-Xylene (E)	115.17	152.22	173.66	185.00	187.45	103.08	
Toluene conv.	41.13	32.59	27.15	23.34	21.44	28.73	
Benzene/xylene (mol)	0.98	0.98	0.00	1.02	1.01	0.00	

**Claims:**

1. A process for the selective production of a para-dialkyl substituted benzene which comprises converting a feedstock comprising

5 (1) a mono-alkyl substituted benzene having an alkyl group of 1 to 4 carbon atoms, or

(2) a mixture of a mono-alkyl substituted benzene or benzene with an alkylating agent containing from 1 to 4 carbon atoms, to a product
10 comprising a para-dialkyl substituted benzene containing alkyl groups of 1 to 4 carbon atoms by contact with a catalyst comprising a porous crystalline material characterized by an X-ray diffraction pattern including the following lines:

15	<u>Interplanar d-Spacing(A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
	12.36 ± 0.4	m-vs
	11.03 ± 0.2	m-s
	8.83 ± 0.14	m-vs
	6.18 ± 0.12	m-vs
20	6.00 ± 0.10	w-m
	4.06 ± 0.07	w-s
	3.91 ± 0.07	m-vs
	3.42 ± 0.06	vs

25 said crystalline material having been treated with a selectivating agent and the treated crystalline material having an Alpha Value of 10 to 2000 and a p-xylene sorption capacity greater than 1 gram/100 grams of crystalline material, said sorption capacity being
30 measured at 120°C and a p-xylene pressure of 4.5 ± 0.8 mm of mercury (600 ± 100 kPa).

2. A process as claimed in claim 1 wherein said crystalline material is selected from MCM-22, MCM-49 and PSH-3.

This Sheet Has Been Replaced

-35-



3. A process as claimed in claim 1 or claim 2 wherein
said crystalline material treatment comprises
contacting said crystalline material with one or a
combination of monomeric or polymeric selectivating
agent compounds and then calcining the contacted
crystalline material.

4. A process as claimed in claim 3 wherein said
contacting is repeated from 2 to 6 times.

5. A process as claimed in any preceding claim wherein
said selectivating agent is a siloxane characterized
by the formula:

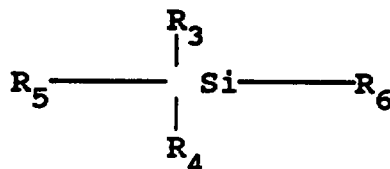


wherein R_1 and R_2 are independently hydrogen; halogen;
hydroxyl; alkyl of from 1 to 10 carbons; halogenated
alkyl of from 1 to 10 carbons; aryl, aralkyl, or
alkaryl of from 6 to 20 carbons; halogenated aryl,
aralkyl, or alkaryl of from 6 to 20 carbons; or
mixtures thereof, and n is an integer of from 2 to
1000.



6. A process as claimed in any preceding claim wherein said selectivating agent is selected from the group consisting of dimethyl silicone, diethyl silicone, phenylmethyl silicone, methylhydrogen silicone, ethylhydrogen silicone, phenylhydrogen silicone, methylethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachlorophenylmethyl silicone, tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen silicone, tetrachlorophenylphenyl silicone, methylvinyl silicone, ethylvinyl silicone, hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, hexaphenyl cyclotrisiloxane and octaphenyl cyclotetrasiloxane, and mixtures thereof.

7. A process as claimed in any one of claims 1 to 4 wherein said selectivating agent is a silane characterized by the formula:

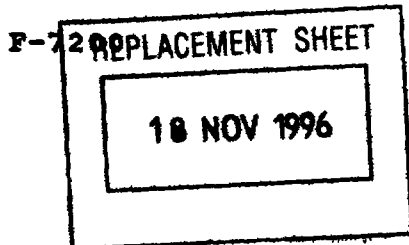


where R_3 , R_4 , R_5 and R_6 are independently selected from the group consisting of hydrogen; hydroxyl; halogen; alkyl of from 1 to 10 carbons; halogenated alkyl of from 1 to 10 carbons; alkoxy of from 1 to 10 carbons; aryl, aralkyl, or alkaryl of from 6 to 20 carbons; halogenated aryl, aralkyl, or alkaryl of from 6 to 20 carbons; organoamine of 3 to 9 carbons; or mixtures thereof.

This Sheet Has Been Replaced -37-



8. A process as claimed in claim 7 wherein said R_3 , R_4 , R_5 , and R_6 are independently selected from the group consisting of $-N(CH_3)_3$, $-N(C_2H_5)_3$, $-N(C_3H_7)_3$, and mixtures thereof.
- 5 9. A process as claimed in any preceding claim wherein the conversion is effected under conditions including a temperature of 100°C to 760°C , a pressure of 10 to 20000 kPa (0.1 to 200 atmosphere), a weight hourly space velocity of 0.08 hr^{-1} to 2000 hr^{-1} and an added
10 hydrogen/hydrocarbon mole ratio of 0 to 100.
10. A process as claimed in any preceding claim wherein the conversion is the disproportionation of toluene and is effected under conditions including a
15 temperature of 200°C to 600°C , a pressure of 100 to 35000 kPa (atmospheric to 5000 psig, a weight hourly space velocity of 0.1 hr^{-1} to 20 hr^{-1} , and an added hydrogen/hydrocarbon mole ratio of 0.05 to 20.



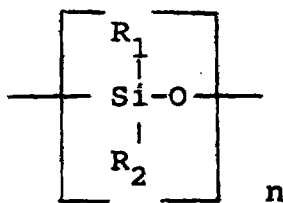
PCT/US 95/05920

-11- 51 Rec'd PCT 06 DEC 1995

is required in order to achieve the desired selective production of para-dialkyl substituted benzenes in this process.

As previously stated, the crystalline material for use herein must be treated with a selectivating agent which alters the diffusion properties of the crystal. Suitable selectivating agents include, for example, silicon-containing compounds such as monomeric or polymeric siloxanes, other main group species (e.g., those containing Ge, B, P, Mg, and/or Sb) which decompose to oxide or non-oxide ceramics, or solid-state carbon species.

Useful selectivating agents include siloxanes which can be characterized by the general formula:



where R_1 is hydrogen; halogen; hydroxyl; alkyl or halogenated alkyl of from 1 to 10 carbons; or aryl, halogenated aryl, aralkyl, halogenated aralkyl, alkaryl or halogenated alkaryl of from 6 to 20 carbons. The hydrocarbon substituents generally contain from 1 to 10 carbon atoms, preferably methyl or ethyl groups. R_2 is independently 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 of the silicone compound employed is generally between 80 and 20,000 and preferably within the range of 150 to 10,000. Representative silicone compounds include dimethyl silicone, diethyl silicone, phenylmethyl silicone, methylhydrogen silicone, ethylhydrogen silicone, phenylhydrogen silicone, methyl-ethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachlorophenylmethyl

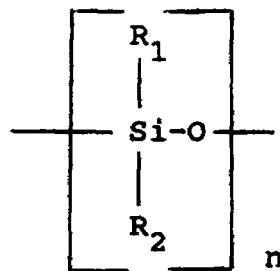
-12- PCT/US 95/05920
06 DEC 1995

The kinetic diameter of the selectivating agent is preferably larger than the zeolite pore diameter, in order

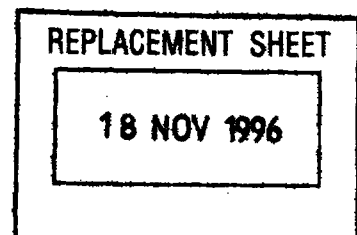


95/05920
06 DEC 1995

3. A process as claimed in claim 1 or claim 2 wherein said crystalline material treatment comprises contacting said crystalline material with one or a combination of monomeric or polymeric selectivating agent compounds and then calcining the contacted crystalline material.
4. A process as claimed in claim 3 wherein said contacting is repeated from 2 to 6 times.
5. A process as claimed in any preceding claim wherein said selectivating agent is a siloxane characterized by the formula:



wherein R_1 and R_2 are independently hydrogen; halogen; hydroxyl; alkyl of from 1 to 10 carbons; halogenated alkyl of from 1 to 10 carbons; aryl, aralkyl, or alkaryl of from 6 to 20 carbons; halogenated aryl, aralkyl, or alkaryl of from 6 to 20 carbons; or mixtures thereof, and n is an integer of from 2 to 1000.



AMENDED SUPPLY



51 Rec'd PCT 06 DEC 1995

8. A process as claimed in claim 7 wherein said R_3 , R_4 , R_5 , and R_6 are independently selected from the group consisting of $-N^+(CH_3)_3$, $-N^+(C_2H_5)_3$, $-N^+(C_3H_7)_3$, and mixtures thereof.
9. A process as claimed in any preceding claim wherein the conversion is effected under conditions including a temperature of 100°C to 760°C , a pressure of 10 to 20000 kPa (0.1 to 200 atmosphere), a weight hourly space velocity of 0.08 hr^{-1} to 2000 hr^{-1} and an added hydrogen/hydrocarbon mole ratio of 0 to 100.
10. A process as claimed in any preceding claim wherein the conversion is the disproportionation of toluene and is effected under conditions including a temperature of 200°C to 600°C , a pressure of 100 to 35000 kPa (atmospheric to 5000 psig), a weight hourly space velocity of 0.1 hr^{-1} to 20 hr^{-1} , and an added hydrogen/hydrocarbon mole ratio of 0.05 to 20.

REPLACEMENT SHEET

18 NOV 1996



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 2/08, 2/12, 5/52		(11) International Publication Number: WO 95/31421
(21) International Application Number: PCT/US95/05920		(43) International Publication Date: 23 November 1995 (23.11.95)
(22) International Filing Date: 11 May 1995 (11.05.95)		(81) Designated States: AU, CA, JP, KR, SG , European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(30) Priority Data: 242,828 16 May 1994 (16.05.94) US		Published With international search report.
(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).		RTMP 54 9611833-6
(72) Inventors: BECK, Jeffrey, Scott; 2411 Town Run North, Lawrenceville, NJ 08648 (US). DESSAU, Ralph, Moritz; 14 Cellar Road, Edison, NJ 08817 (US).		
(74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		
(54) Title: SELECTIVE PRODUCTION OF PARA-DIALKYL SUBSTITUTED BENZENES		
(57) Abstract A process is provided for selective catalytic conversion of certain hydrocarbon feedstocks to product rich in para-dialkyl substituted benzenes. The catalyst employed in the process comprises a crystalline material having the structure of PSH-3, MCM-22 or MCM-49, or a mixture of said crystalline materials, said crystalline material having been treated with a selectivating agent, such as a silicon compound, which decomposes to oxide or non-oxide ceramic or solid-state carbon species.		

FOR THE PURPOSES OF INFORMATION ONLY

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

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

9611833-6