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54	A PROCESS FOR PRODUCING TEREPHTHALIC ACID AND/OR DIMETHYL TEREPHTHALATE

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(57) Abstract

A process for producing terephthalic acid and/or dimethyl terephthalate includes contacting a toluene-containing reaction stream with a first catalyst under toluene disproportionation conditions to produce an intermediate product stream of para-xylene with negligible ortho-xylene. The first catalyst includes a crystalline molecular sieve which has an ortho-xylene diffusion rate of at least 50 minutes. The first catalyst can be modified by selectivation with a silicon compound or carbon compound. The intermediate product stream, without need for para-xylene purification, is oxidized to terephthalic acid or dimethyl terephthalate.

A PROCESS FOR PRODUCING TEREPHTHALIC ACID AND/OR DIMETHYL TEREPHTHALATE

The invention relates to a process integrating p-xylene production with terephthalic acid and/or dimethyl terephthalate production without need for intermediate purification of p-xylene

Para-xylene is oxidized to produce terephthalic acid or dimethyl terephthalate which are polymerized to yield polyester fibers and films. Processes for the production of terephthalic acid (1,4-benzenedicarboxylic acid) and dimethyl terephthalate are well known and described, e.g., in U.S. Patent No. 2,833,816 and British Patent Specification Nos. 809,730 and 727,989.

Of the three xylene isomers, meta, ortho and para, only p-xylene is suitable for the production of terephthalic acid and/or dimethyl terephthalate for polyester manufacture because of the ability of p-xylene to form straight polymer chains. Straight claims are necessary to give polyester its fiber-forming or film-forming characteristics and high tensile strength.

The p-xylene must be substantially pure to avoid unwanted side reactions when the p-xylene is oxidized to terephthalic acid.

Para-xylene has been typically produced by methylation of toluene, e.g., by reaction of toluene with methanol as generally described by Chen et al., *J. Am. Chem. Soc.* 1979, 101:6783, and by toluene disproportionation, e.g., as generally described by Pines in *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York 1981, p. 72. Such methods typically produce a mixture of C₈ products including para-xylene, ortho-xylene, meta-xylene and ethylbenzene. Para-xylene may be recovered from mixed C₈ streams followed by xylene isomerization of the remaining stream as described, e.g., in U.S. Patent Nos. 3,856,871 and Re 31,782.

In terephthalic acid production, one unwanted by-product results from the presence of o-xylene in the xylene feed. Any o-xylene present is oxidized to orthophthalic acid and subsequently dehydrated to phthalic anhydride, interfering with terephthalic acid production and impacting on the oxidation catalyst lifetime. If ethylbenzene (EB), another C₈, is present in the p-xylene feed for terephthalic acid production, the EB may be oxidized to benzoic acid. Meta-xylene is oxidized to isophthalic acid. These oxidation products are more easily

separated from PTA than the oxidation products of o-xylene. The quality of polyester is affected by even small amounts of organic or inorganic impurities which cause process difficulties during polymerization and affect the color, thermal and photochemical stability, and long-term durability of the polyester product. The precursor for polyester production is purified terephthalic acid (PTA). Further, the PTA thus produced may be esterified with an alcohol, e.g., reaction of PTA with methanol yields dimethyl terephthalate which may also be used in polyester production.

As disclosed, e.g., in British Patent Specification No. 727,989, if the initial p-xylene feed does not consist of pure para-xylene compound but also contains other xylene isomers and/or non-aromatic compounds, a purification of the feed is necessary. Purification of the p-xylene feed is generally carried out using physical processes such as fractional distillation or crystallization described, e.g., in U.S. Patent Nos. 3,177,255 and 3,467,724, absorption described, e.g., in U.S. Patent No. 2,985,589, or chemical processes, e.g., contacting with formaldehyde in acid solution which removes m-xylene as a resin. A widely used method is UOP's PAREX® process described by J.J. Jeanneret, "UOP Parex Process," in *Handbook of Petroleum Refining Processes*, R.A. Meyers, ed., McGraw-Hill, NY, 1997. Other methods for separating p-xylene from a C₈ aromatic mixture are described by U.S. Patent No. 4,705,909. In conventional xylene manufacture, significant costs are incurred for p-xylene purification for PTA production.

It is an object of the invention to improve terephthalic acid and/or dimethyl terephthalate manufacture by minimizing unwanted oxidation by-products. It is another object of the invention to eliminate the need for a purification process for p-xylene to be used in terephthalic acid and/or dimethyl terephthalate production.

According to the invention, there is provided a process for producing terephthalic acid and/or dimethyl terephthalate comprising the steps of:

- (a) contacting a reaction stream comprising toluene under toluene disproportionation conditions with a first catalyst wherein the first catalyst comprises a crystalline molecular sieve having an ortho-xylene diffusion time of greater than 50 minutes, said first contacting producing para-xylene product, and
- (b) contacting the product of (a) with a second catalyst under oxidizing conditions to produce terephthalic acid and/or dimethyl terephthalate.

In the process of the invention, the first contacting step produces an intermediate product stream containing p-xylene with negligible or essentially no ortho-xylene and negligible or essentially no ethylbenzene (EB). The intermediate product stream containing p-xylene is oxidized to terephthalic acid in a second contacting with a second catalyst. There is no need for purification of the intermediate product stream to remove ortho-xylene or EB. The second catalyst is any catalyst which catalyzes oxidation of p-xylene to terephthalic acid, e.g., heavy metal catalyst such as cobalt and/or manganese, and which optionally may include a catalyst for esterification to dimethyl terephthalate.

Advantageously, a costly xylene separation step is eliminated and the product stream of the first contacting can be directly integrated with the oxidation process to pure terephthalic acid or dimethyl terephthalate.

Catalyst System

Catalysts useful for the production of p-xylene in this invention may comprise crystalline molecular sieves having the specified ortho-xylene diffusion rate, e.g., zeolites, ALPO₄'s, SAPO's or combinations of these.

Examples of crystalline molecular sieves useful in this invention include intermediate pore size zeolites ZSM-5 (U.S. Patent Nos. 3,702,886 and Re,29,948); ZSM-11 (U.S. Patent No. 3,709,979); ZSM-12 (U.S. Patent No. 3,832,449); ZSM-22 (U.S. Patent No. 4,556,477); ZSM-23 (U.S. Patent No. 4,076,842); ZSM-35 (U.S. Patent No. 4,016,245); ZSM-48 (U.S. Patent No. 4,397,827); ZSM-57 (U.S. Patent No. 4,046,685); and ZSM-58 (U.S. Patent No. 4,417,780). Also useful are silicoaluminophosphates (SAPO's), particularly SAPO-5 and SAPO-11 (U.S. Patent No. 4,440,871) and aluminophosphates (ALPO₄'s), particularly ALPO₄-5, and ALPO₄-11 (U.S. Patent No. 4,310,440). Intermediate pore size zeolites generally have a Constraint Index within the approximate range of 1 to 12 (e.g., zeolites having less than 7 Angstroms pore size, such as from 5 to less than 7 Angstroms). Preferred intermediate pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-35 and MCM-22. Most preferred is ZSM-5.

When ZSM-5 is used as the toluene conversion catalyst of this invention, it may comprise a medium or large crystal size. If another intermediate pore size zeolite is used as the toluene conversion catalyst, the crystal size may need to be adjusted from those given above for best performance.

The crystalline molecular sieve may be used in bound or unbound form, but preferably is bound with silica. In addition the catalyst can be silicon selectivated through ex situ methods of impregnation or multiple impregnation or in situ methods of trim selectivation; or coke selectivated; or combination of these, to result in the desired ortho-
5 xylene diffusion rate.

Procedures for preparing silica bound ZSM-5 are described in U.S. Patent Nos. 4,582,815; 5,053,374 and 5,182,242. A particular procedure for binding ZSM-5 with a silica binder involves an extrusion process. The catalyst may be a zeolite bound zeolite as described in U.S. Patent No. 5,665,325.

10 There are various methods for increasing the selectivity of zeolite catalysts. One such method is to modify the catalyst by treatment with a "selectivating agent." For example, U.S. Patent Nos. 5,173,461; 4,950,835; 4,927,979; 4,465,886; 4,477,583; 4,379,761; 4,145,315; 4,127,616; 4,100,215; 4,090,981; 4,060,568 and 3,698,157 disclose specific methods for contacting a catalyst with a selectivating agent containing silicon
15 ("silicon compound"). Also, U.S. Patent Nos. 5,367,099; 5,382,737; 5,365,004; 5,403,800; 5,406,015 and 5,476,823 disclose methods for silicon selectivation of catalysts and use of those catalysts in toluene and ethylbenzene disproportionation.

In accordance with one selectivation method (first method), the multiple impregnation method, the catalyst is selectivated by one or more treatments with a liquid
20 organosilicon compound in a liquid carrier, each treatment being followed by calcination of the treated material in an oxygen containing atmosphere, e.g., air. More particularly, for example, with reference to the above-mentioned steps (i)-(iii), this first selectivation method may involve the additional steps of:

(iv) contacting the calcined extrudate of step (iii) with a liquid comprising a liquid
25 carrier and at least one organosilicon selectivating agent having at least two silicon atoms per molecule under conditions sufficient to incorporate said organosilicon selectivating agent in the extrudate.

(v) calcining the extrudate of step (iv) under conditions sufficient to decompose said organosilicon selectivating agent and to remove any residue of said liquid carrier from
30 said extrudate; and, optionally,

(vi) repeating selectivation steps (iv) and (v) at least once.

Another method (second method) for selectivating the catalyst, trim-selectivation, involves passing a feed stream comprising hydrogen and an aromatic (e.g., toluene) or a paraffin (e.g., hexane or decane) and an organosilicon compound over HZSM-5, e.g., silica bound ZSM-5, under conditions sufficient to deposit a residue of organosilicon compound on the ZSM-5.

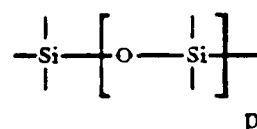
The above-mentioned first method for selectivating the zeolite, wherein the zeolite, e.g., HZSM-5, is treated by multiple impregnation treatments, is referred to herein as the multiple impregnation method. The above-mentioned second method for selectivating the zeolite, wherein the zeolite, e.g., HZSM-5, is treated under trim-selectivation conditions, is referred to herein as the trim-selectivation method. Another method (third method) for selectivating the zeolite, described herein, which includes decomposing an organic compound on and in the zeolite, is referred to herein as the coke selectivation method. The present catalyst may be selectivated by any of the above selectivation methods or by more than one selectivation method used in combination.

In accordance with the multiple impregnation method, the zeolite, e.g., HZSM-5, is treated at least once, e.g., at least twice, e.g., 3 times or more, e.g., from 4 to 6 times, with a liquid medium comprising a liquid carrier and at least one liquid organosilicon compound. The organosilicon compound may be present in the form of a solute dissolved in the liquid carrier or in the form of emulsified droplets in the liquid carrier. For the purposes of the present disclosure, it will be understood that a normally solid organosilicon compound will be considered to be a liquid (i.e., in the liquid state) when it is dissolved or emulsified in a liquid medium. The liquid carrier may be water, an organic liquid or a combination of water and an organic liquid. Particularly when the liquid medium comprises an emulsion of the organosilicon compound in water, the liquid medium may also comprise an emulsifying agent, such as a surfactant. As mentioned above, the zeolite may be silica bound before selectivation, after selectivation, or between successive selectivation coatings.

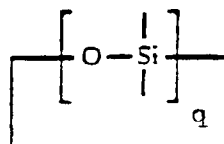
The organosilicon compound which is used to selectivate the zeolite may be a silicone, siloxane or a silane. Silicones are defined herein as those compounds wherein silicon atoms are bonded to one another via oxygen atoms. Silanes are defined herein as those compounds wherein silicon atoms are bonded directly to one another. The organosilicon compound preselectivating agent may be, for example, a silicone, a siloxane, a

silane or mixtures thereof. These organosilicon compounds may have at least 2 silicon atoms per molecule. These organosilicon compounds may be solids in pure form, provided that they are soluble or otherwise convertible to the liquid form upon combination with the liquid carrier medium. The molecular weight of the silicone, siloxane or silane compound employed as a preselectivating agent may be between 80 and 20,000 and preferably within the approximate range of 150 to 10,000.

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 zeolite pores and any concomitant reduction in the internal activity of the zeolite. The silicone compound which may be used to selectivate the present zeolite may be considered to be constructed of a siloxy backbone structure capped with terminal groups. This siloxy backbone structure may be a chain structure represented by the formula:



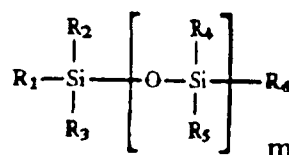
where p is from 1 to 100, e.g., 1 to 25 e.g., 1 to 9. This siloxy backbone structure may also be a cyclic structure represented by the formula:



where q is from 2 to 10. Branched chain structures and composite chain/cyclic structures are also possible for the siloxy backbone of the silicone selectivating agent.

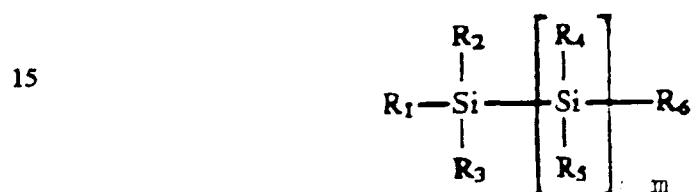
The hydrocarbyl groups which cap the available bonds of the siloxy backbone may have from 1 to 10 carbon atoms. Examples of such hydrocarbyl groups are methyl and phenyl.

Examples of silicone compounds having a chain siloxy backbone structure include those of the formula:



where R_1 and R_6 are independently hydrogen, methyl, or phenyl; R_2 , R_3 , R_4 and R_5 are independently methyl or phenyl; and m is from 1 to 100, e.g., from 1 to 25, e.g., from 1 to 10, e.g., from 1 to 4. Preferably, no more than one phenyl group is bonded to each silicon atom. Particular examples of such silicone compound having a chain siloxy backbone structure include hexamethyldisiloxane, decamethyltetrasiloxane and diphenyltetramethyl-
 5 disiloxane. Particular examples of silicone compounds having a cyclic siloxy backbone structure include octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane. Particular examples of silicone compounds having a branched siloxy backbone structure are tris-(trimethylsiloxy)-phenylsilane and tris-(trimethylsiloxy)-silane.

10 The silane compounds, useful as selectivating agents according to the present method, may have structures corresponding to the above-mentioned silicone compounds, wherein the silicon atoms are bonded directly to one another instead of via oxygen atoms. Examples of silanes having a chain backbone structure include those of the formula:



where R_1 and R_6 are independently hydrogen, methyl, or phenyl; R_2 , R_3 , R_4 and R_5 are independently methyl or phenyl; and m is from 1 to 100, e.g., from 1 to 25, e.g., from 1 to 10, e.g., from 1 to 4. An example of such a silane compound is hexamethyldisilane.

Representative preselectivation silicone compounds include dimethyl silicone, diethyl silicone, phenylmethyl silicone, methylhydrogen silicone, ethylhydrogen silicone, phenylhydrogen silicone, methylethyl silicone, phenylethylsilicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachlorophenylmethyl silicone, tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen
 25 silicone, tetrachlorophenylphenyl silicone, methylvinyl silicone, and ethylvinyl silicone. The preselectivating silicone, siloxane or silane 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
 30 be used as preselectivating agents, as may silicones with other functional groups.

Preferred organosilicon preselectivating agents, particularly when the preselectivating agent is dissolved in an organic carrier or emulsified in an aqueous carrier, include dimethylphenyl methyl polysiloxane (e.g., Dow-550) and phenylmethyl polysiloxane (e.g., Dow-710). Dow-550 and Dow-710 are available from Dow Chemical Co., Midland, MI.

5 When the organosilicon preselectivating agent is present in the form of a water soluble compound in an aqueous solution, the organosilicon may be substituted with one or more hydrophilic functional groups or moieties, which serve to promote the overall water solubility of the organosilicon compound. These hydrophilic functional groups may include one or more organoamine groups, such as $-N(CH_3)_3$, $-N(C_2H_5)_3$ and $-N(C_3H_7)_3$. A preferred
10 water soluble organosilicon preselectivating agent is an n-propylamine silane, available as Hydrosil 2627 from Huls America. Particular water soluble organosilicon compounds, which may be used for multiple impregnations of the present catalyst, are referred to as amino silane polymers in U.S. Patent No. 5,371,312. As mentioned previously herein, aqueous emulsions of organosilicon compounds comprising surfactants may be used for the
15 impregnation of the present catalyst. Stable aqueous emulsion of organosilicon compounds (e.g., silicone oil) are described in U.S. Patent No. 5,726,114.

The first catalyst may be selectivated by more than one selectivation method. In particular, prior to use in the present process, the crystalline molecular sieve may be contacted with an organosilicon compound, followed by calcination in an oxygen containing
20 atmosphere. Such a pretreatment of the molecular sieve may also be referred to herein as a preselectivation treatment.

In accordance with an example of a preselectivation method, the catalyst is preselectivated by single or multiple treatments with a liquid organosilicon compound in a liquid carrier, each treatment being followed by calcination of the treated material in an
25 oxygen containing atmosphere, e.g., air.

When the catalyst is preselectivated by a single or multiple impregnation technique, the catalyst is calcined after each impregnation to remove the carrier and to convert the liquid organosilicon compound to a solid residue material thereof. This solid residue material is referred to herein as a siliceous solid material, insofar as this material is believed to be a
30 polymeric species having a high content of silicon atoms in the various structures thereof. However, this siliceous solid residue material may also comprise carbon atoms in the

structure thereof, resulting from the residue of the organo portion of the organosilicon compound used to impregnate the catalyst.

Following each impregnation, the catalyst may be calcined at a rate of from 0.2°C/minute to 5°C/minute to a temperature greater than 200°C, but below the temperature at which the crystallinity of the crystalline molecular sieve is adversely affected. This
5 calcination temperature may be below 700°C, e.g., within the approximate range of 350°C to 550°C. The duration of calcination at the calcination temperature may be from 1 to 24 hours, e.g., from 2 to 6 hours.

The impregnated catalyst may be calcined in an inert or oxidizing atmosphere. An
10 example of such an inert atmosphere is nitrogen, i.e., N₂, atmosphere. An example of an oxidizing atmosphere is an oxygen-containing atmosphere, such as air. Calcination may take place initially in an inert, e.g., N₂, atmosphere, followed by calcination in an oxygen-containing atmosphere, such as air or a mixture of air and N₂. Calcination should be performed in an atmosphere substantially free of water vapor to avoid undesirable
15 uncontrolled steaming of the catalyst. The catalyst may be calcined once or more than once following each impregnation. The various calcinations following each impregnation need not be identical, but may vary with respect to the temperature, the rate of temperature rise, the atmosphere and the duration of calcination.

The amount of siliceous residue material which is deposited on the molecular sieve or
20 bound molecular sieve is dependent upon a number of factors including the temperatures of the impregnation and calcination steps, the concentration of the organosilicon compound in the carrying medium, the degree to which the catalyst has been dried prior to contact with the organosilicon compound, the atmosphere used in the calcination and the duration of the calcination. A suitable amount of silicon on the catalyst is greater than 9 weight percent
25 (wt.%), e.g., greater than 12 wt.%, exclusive of the silica present in the binder or in the crystalline molecular sieve itself.

In accordance with the trim-selectivation method described herein, the first catalyst may be contacted with a feed stream typically comprising hydrogen and an aromatic compound (e.g., toluene) or a paraffinic compound (e.g., hexane or decane) with the
30 organosilicon compound under suitable trim selectivation conditions. These conditions may include a temperature ranging from 100°C to 600°C, e.g., from 300°C to 500°C, a pressure

ranging from 0 to 2000 psig, e.g., from 15 to 800 psig, a mole ratio of hydrogen to hydrocarbons (e.g., toluene) from 0.1 to 20 e.g., from 0.25 to 10, e.g., from 1 to 4, and a weight hourly space velocity (WHSV) from 0.1 to 100 hr⁻¹, e.g., from 0.1 to 10 hr⁻¹.

5 Toluene may comprise 50 wt.% to 100 wt.%, e.g., at least 80 wt.% of the hydrocarbons in the feedstock. Other hydrocarbons, such as benzene, xylenes and trimethylbenzenes, may also be present in the trimselectivation feedstock.

The presence of a sufficient amount of hydrogen in the trim-selectivation feedstock is helpful to prevent rapid aging of the catalyst during the selectivation process, a small amount of carbonaceous deposit may form on the catalyst. As a result of this carbonaceous deposit,
10 an elemental analysis of the trim-selectivated catalyst may reveal a carbon content significantly greater than the carbon content of the fresh catalyst prepared by the multiple impregnation method described herein. More particularly, the trim-selectivated catalyst may contain at least 2 wt.%, e.g., at least 4 wt.%, of carbon by elemental analysis, whereas the catalyst prepared by the multiple impregnation method may contain less than 0.5 wt.% of
15 carbon as measured by elemental analysis. These weight percentages are expressed in terms of the weight of the entire catalyst including the crystalline molecular sieve, binder and optional components, such as hydrogenation/dehydrogenation components.

The first catalyst may also be subjected to controlled coking. This controlled coking procedure is also referred to herein as coke selectivation. This optional coke selectivation
20 may involve contacting the catalyst with a thermally decomposable organic compound at an elevated temperature in excess of the decomposition temperature of said compound but below the temperature at which the crystallinity of the zeolite is adversely affected. This contact temperature may be, for example, less than 650°C. The catalyst may be coked in a reactor or other vessel that is different than that used for the toluene conversion, followed by
25 transport of the coked catalyst to the toluene conversion reactor.

Organic materials, which may be used for this coke selectivation process, encompass a wide variety of compounds including by way of example, hydrocarbons, such as paraffins, cycloparaffins, olefins, cycloolefins and aromatics; oxygen-containing organic compounds, such as alcohols, aldehydes, ethers, ketones and phenols; and heterocyclics, such as furans,
30 thiophenes, pyrroles and pyridines. A hydrogen cofeed may be used to deter the excessive build-up of coke. Further details regarding coke selectivation techniques are provided in the

U.S. Patent Nos. 4,117,026 and 5,476,823. An organosilicon cofeed may be, optionally, included along with the organic material feed used for coke selectivation. This organosilicon material may be selected from the organosilicon compounds mentioned hereinabove for use in the selectivation of the catalyst.

5 While it is not intended to be bound by any particular theory, it is possible that the selectivity of the present catalyst is obtained by producing changes in the diffusion properties of the zeolite that favor the desired reactions and inhibit undesired reactions.

The crystalline molecular sieve component of catalysts suitable for use as the first catalyst may be characterized by different xylene diffusion properties or xylene sorption capabilities. In particular, it has been found that the first catalyst should possess an
10 equilibrium sorption capacity of xylene, which can be either para, meta, ortho or a mixture thereof, frequently para-xylene, since this isomer reaches equilibrium within the shortest time, of at least 1 gram per 100 grams of zeolite measured at 120°C and a xylene pressure of 4.5±0.8 mm of mercury and an ortho-xylene sorption time for 30 percent of the xylene
15 sorption capacity of greater than 50, preferably greater than 200, more preferably greater than 1200 (at the same conditions of temperature and pressure) are required in order to achieve the desired level of para-xylene selectivity at appropriate toluene conversion. The sorption measurements may be carried out gravimetrically in a thermal balance.

It has been found that zeolites exhibiting very high selectivity for para-xylene while
20 minimizing ortho xylene require a very long time, preferably up to and exceeding 1200 minutes to sorb ortho-xylene in an amount of 30% of total xylene sorption capacity. For those materials, it may be more convenient to determine the sorption time for a lower extent of sorption, such as 5%, 10% or 20% of capacity, and then to estimate the 30% sorption time by applying the following multiplication factor, F, as illustrated for 5% sorption:

25
$$t_{0.3} = F \cdot t_{0.05}$$

Percent of sorption capacity	Factor, F, to estimate 30% sorption time, $t_{0.3}$
5	36
10	9
20	2.25

30

Alternatively, $t_{0.3}$ may be calculated for other sorption times at less than 30% of xylene capacity using the following relationship:

$$t_{0.3} = t_{0.x} (0.3/0.x)^2$$

where

5 $t_{0.3}$ - sorption time for 30% of total xylene capacity

$t_{0.x}$ - sorption time for x% of total xylene capacity

0.x - fractional amount of ortho-xylene sorption to total xylene capacity

In accordance with the invention, the crystalline molecular sieve component of the catalyst that is effective for the toluene conversion may have a $t_{0.3}$ value (in minutes) for
10 ortho-xylene in excess of 50, e.g., greater than 200, e.g., greater than 1200 minutes.

Toluene Disproportionation

The first catalyst can be contacted with a toluene feedstock under conditions for effecting disproportionation. Conditions effective for accomplishing high p-xylene selectivity and acceptable toluene conversion levels include a reactor inlet temperature of from 200°C
15 (392°F) to 550°C (1022°F), preferably from 312°C (600°F) to 532°C (1000°F); a pressure from atmospheric to 5000 psi, preferably 20 to 1000 psig; a WHSV from 0.1 to 20, preferably from 0.5 to 10; and a H₂/hydrocarbon mole ratio from 0 to 20, preferably from 0 to 10. This process may be conducted in either continuous flow, batch or fluid bed operation.

The catalyst can be further modified to reduce undesirable amounts of by-products,
20 particularly ethylbenzene, by incorporating a hydrogenation/dehydrogenation function within the catalyst, such as by the addition of a metal compound such as platinum or other metals of Groups 4 to 13 of the Periodic Table, such as platinum, palladium, silver, gold, copper, zinc, nickel, gallium, cobalt, molybdenum, rhodium, ruthenium, manganese, rhenium, tungsten, chromium, iridium, osmium, iron, cadmium, and mixtures (combinations) thereof. The metal
25 may be added by cation exchange or by impregnation by known methods in amounts of from 0.01% to 10%, typically 0.05% to 10%.

Toluene disproportionation over the selectivated catalyst shown selectivity toward a high-purity p- and m-xylene product. It is possible to achieve a xylene product with virtually no o-xylene at toluene conversion levels as high as 27%. A C₈ stream can be produced
30 with no o-xylene, blended to reduce o-xylene, or a stream can be taken through a o-xylene splitter to prepare a C₈ feed to a purified terephthalic acid unit. The xylene product

preferably includes essentially no o-xylene or negligible o-xylene. By negligible is meant less than 0.2%, preferably less than 0.1%, more preferably less than 0.05%. It has been found that such a xylene product can be fed directly to the terephthalic acid production step without intermediate purification.

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Terephthalic Acid Production

A number of processes are used commercially in the production of terephthalic acid. One is the Amoco process described, e.g., in U.S. Patent No. 2,833,816. This process involves liquid phase air oxidation of p-xylene using multivalent (heavy) metals, particularly cobalt and manganese as catalyst in an acetic acid solvent and with bromine as a renewable
10 source of free radicals. The terephthalic acid product crystals are recovered, e.g., by centrifugation, and purified by dissolving the crystals in water contacting with a hydrogenation catalyst, e.g., noble metal on a carbon support, and again recovering the crystals. Dimethyl terephthalate can be produced by liquid phase esterification of the terephthalic acid using metal catalysts such as zinc, molybdenum, antimony and tin with a
15 large excess of methanol.

In another process, four steps are used, alternating oxidation and esterification to produce dimethyl terephthalate, as described, e.g., in British Patent Specification Nos. 727,989 and 809,730. First, p-xylene is oxidized with a molecular oxygen-containing gas (air) in a liquid phase in the presence of a heavy metal catalyst such as cobalt, manganese, or
20 mixture of both to produce p-toluic acid (PTA) which is esterified with methanol to produce methyl p-toluate (MPT). A second oxidation of the MPT with the same catalyst and molecular oxygen yields in a liquid phase yields monomethyl terephthalate which is esterified to the diester dimethyl terephthalate.

Both terephthalic acid and dimethyl terephthalate are used in the production of
25 polyethylene terephthalate (PET) or other polyesters through a reaction with glycol, e.g., ethylene glycol or tetramethylene glycol.

The invention is illustrated by the following non-limiting example.

EXAMPLE

A catalyst was manufactured by multiple silica selectivation of a ZSM-5 containing
30 extrudate (65% zeolite/35% silica). Selectivation of the catalyst was carried out using the pore filling technique contacting the catalyst four times with 7.8% organosilicone fluid

(Dow-550, Dow Chemical Co., Midland, MI) dissolved in decane and twice more with 2% organosilicone fluid, followed by hybrid calcination in nitrogen/air.

Catalyst evaluations were performed by loading 2g of extrudate, mixed with sand as a packing material, into a 3/8" OD reactor tube. The catalyst was then heated to reaction temperature under nitrogen, at which time, a mixed hydrogen/toluene feed is introduced. Sample analyses were acquired via on-line gas chromatography (GC). Operating conditions and yields are shown below in Table 1.

TABLE 1

Temp (°F)	734	752	769	787	805
Press (Psig)	275	275	275	275	275
WHSV	3	3	3	3	3
H ₂ /HC	1	1	1	1	1
<u>Yields (Wt.%)</u>					
C ₅ -	0.36	0.51	0.75	1.02	1.47
Benzene	6.79	7.81	9.64	11.86	13.71
Ethylbenzene	0.10	0.16	0.22	0.31	0.39
p-xylene	7.60	9.37	9.94	10.64	10.76
m-xylene*	-	0.09	0.13	0.17	0.22
o-xylene*	-	-	-	-	-
C ₉ +	0.20	0.26	0.27	0.32	0.37
p-Selectivity	{100}	99.07	98.70	98.43	98.04
p-Purity	98.7	97.40	96.59	95.68	94.63
Toluene					
Conversion	15.1	18.28	21.02	24.42	27.02

* Where no accurate measurement of concentration can be obtained in the present gas chromatographic technique, a value of less than 100 ppm is estimated.

An optimum level of toluene conversion is selected and a product slate is selected in which the C₈ fraction is essentially all p-xylene. This stream can be used directly (no crystallization or sorption process required to purify the p-xylene) to a Purified Terephthalic Acid (PTA) unit for oxidation and subsequent esterification.

CLAIMS:

1. A process for producing terephthalic acid or dimethyl terephthalate comprising:
 - 5 (a) contacting a reaction stream comprising toluene under toluene disproportionation conditions with a first catalyst wherein the first catalyst comprises a crystalline molecular sieve having an ortho-xylene diffusion time of greater than 50 minutes, said first contacting producing para-xylene product, and
 - (b) contacting the product of (a) with a second catalyst under oxidizing
10 conditions to produce terephthalic acid and/or dimethyl terephthalate.
2. The process of Claim 1 wherein the first catalyst comprises an intermediate pore zeolite, a SAPO, an ALPO₄ or combination thereof.
- 15 3. The process of Claim 2 wherein the intermediate pore zeolite has a Constraint Index ranging from 1 to 12.
4. The process of Claim 1 wherein the toluene disproportionation conditions comprise a temperature from 600°F to 1000°F, a pressure from 20 to 1000 psi, a WHSV of
20 0.5 to 20, and hydrogen/hydrocarbon mole ratio of 0 to 10.
5. The process of Claim 1 wherein the first catalyst has been subject to modification by exposure to a silicon compound or a carbon compound.
- 25 6. The process of Claim 5 wherein the modification is ex situ silicon selectivation by impregnation or multiple impregnation, in situ silicon trim selectivation, carbon selectivation, or combinations thereof.
7. The process of Claim 1 wherein contacting step (b) comprises liquid phase
30 oxidation.

8. The process of Claim 1 wherein the para-xylene product of step (a) contains negligible ortho-xylene and is fed directly to step (b) without intermediate purification.