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CASE 2288

CONVENTION

TITLE:

"C₈ AROMATICS ISOMERIZATION USING
CATALYST CONTAINING MODIFIED
SILICOALUMINOPHOSPHATE MOLECULAR SIEVE"

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"C₈ AROMATICS ISOMERIZATION USING CATALYST CONTAINING
MODIFIED SILICOALUMINOPHOSPHATE MOLECULAR SIEVE"

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BACKGROUND

10 Molecular sieves having a wide variety of compositions and structures have been disclosed in the art as useful in catalysts for hydrocarbon conversion. The most well known are the crystalline aluminosilicate zeolites formed from corner-sharing AlO₂ and SiO₂ tetrahedra. The zeolites generally feature pore openings of uniform dimensions, significant ion-exchange capacity and the capability of reversibly desorbing an adsorbed phase which is dispersed throughout the internal voids of the crystal without displacing any atoms which make up the permanent crystal structure. Zeolites
15 often are characterized by a critical, usually minimum, silica/alumina ratio.

More recently, a class of useful non-zeolitic molecular sieves containing framework tetrahedral units (TO₂) of aluminum (AlO₂), phosphorus (PO₂) and at least one additional element EL (ELO₂) has been disclosed. "Non-zeolitic molecular sieves" include the "ELAPSO" molecular sieves as disclosed in US-A-4793984 and "SAPO"
20 molecular sieves of US-A-4440871. Generally the above patents teach a wide range of framework metal concentrations, e.g., the mole fraction of silicon in. '871 may be between 0.01 and 0.98 depending on other framework elements with a preferable range of 0.02 to 0.25 mole fraction. US-A-4943424 discloses a silicoaluminophosphate molecular sieve characterized by surface and bulk P₂O₅-to-alumina ratios in the surface and bulk of the sieve and silicon content of the surface and its use in dewaxing and
25 hydrocracking.

US-A-4740650 teaches xylene isomerization using a catalyst containing at least one non-zeolitic molecular sieve which preferably is a silicoaluminophosphate. This '650 patent does not suggest the critical composition gradients which are a feature of
30 the modified molecular sieve used in the present invention.

Catalysts for isomerization of C₈ aromatics ordinarily are classified by the manner of processing ethylbenzene associated with the xylene isomers. Ethylbenzene

is not easily isomerized to xylenes, but it normally is converted in the isomerization unit because separation from the xylenes by superfractionation or adsorption is very expensive. A widely used approach is to dealkylate ethylbenzene to form principally benzene while isomerizing xylenes to a near-equilibrium mixture. An alternative approach is to react the ethylbenzene to form a xylene mixture via conversion to and reconversion from naphthenes in the presence of a solid acid catalyst with a hydrogenation-dehydrogenation function. The former approach commonly results in higher ethylbenzene conversion, thus lowering the quantity of recycle to the para-xylene recovery unit and concomitant processing costs, but the latter approach enhances xylene yield by forming xylenes from ethylbenzene. A catalyst composite and process which enhance conversion according to the latter approach, i.e., achieve ethylbenzene isomerization to xylenes with high conversion, would effect significant improvements in xylene-production economics.

SUMMARY

A principal object is to provide a novel isomerization process for alkylaromatic hydrocarbons. More specifically, this invention is directed to isomerization of C₈-aromatic hydrocarbons using a critically defined molecular-sieve catalyst to obtain improved xylene yields.

This invention is based on the discovery that a catalyst comprising a SAPO molecular sieve having enriched surface silicon demonstrates improved conversion and selectivity in alkylaromatic, C₈-aromatics, particularly isomerization.

Accordingly, a broad embodiment of the invention is directed toward an alkylaromatics-isomerization process using a silicoaluminophosphate (SAPO) molecular-sieve catalyst having an enriched framework surface-silicon content. The process comprises isomerization with this catalyst of a feedstock comprising a non-equilibrium mixture of xylenes and ethylbenzene at isomerization conditions to obtain a product having an increased para-xylene content relative to that of the feedstock. Preferably this SAPO-containing catalyst comprises a platinum-group metal, with

platinum being an especially preferred component. The optimal catalyst composite also comprises an inorganic-oxide binder, usually alumina and/or silica.

DETAILED DESCRIPTION

5 The feedstock to an aromatics isomerization process typically comprises isomerizable alkylaromatic hydrocarbons of the general formula $C_6H_{(6-n)}R_n$, where n is an integer from 1 to 5 and R is CH_3 , C_2H_5 , C_3H_7 , or C_4H_9 , in any combination and including all the isomers thereof to obtain more valuable isomers of the alkylaromatic. Suitable alkylaromatic hydrocarbons include, for example but without so limiting the
10 invention, ortho-xylene, meta-xylene, para-xylene, ethylbenzene, ethyltoluenes, trimethylbenzenes, di-ethylbenzenes, tri-ethyl-benzenes, methylpropylbenzenes, ethylpropylbenzenes, di-isopropylbenzenes, and mixtures thereof.

Isomerization of a C_8 -aromatic mixture containing ethylbenzene and xylenes is a particularly preferred application of the SAPO sieves of the invention. Generally
15 such mixture will have an ethylbenzene content in the approximate range of 5 to 50 mass-%, an ortho-xylene content in the approximate range of 0 to 35 mass-%, a meta-xylene content in the approximate range of 20 to 95 mass-% and a para-xylene content in the approximate range of 0 to 15 mass-%. It is preferred that the aforementioned C_8 aromatics comprise a non-equilibrium mixture, i.e., at least one C_8 -aromatic isomer
20 is present in a concentration that differs substantially from the equilibrium concentration at isomerization conditions. Usually the non-equilibrium mixture is prepared by removal of para- and/or ortho-xylene from a fresh C_8 aromatic mixture obtained from an aromatics-production process.

The source of the alkylaromatic hydrocarbons feed may be found in appropriate
25 fractions from various refinery petroleum streams, e.g., as individual components or as certain boiling-range fractions obtained by the selective fractionation and distillation of catalytically cracked or reformed hydrocarbons. The isomerizable aromatic hydrocarbons need not be concentrated; this invention allows the isomerization of alkylaromatic-containing streams such as catalytic reformat with or without subsequent
30 aromatics extraction to produce specified xylene isomers and particularly to produce

para-xylene. A C₈-aromatics feed may contain nonaromatic hydrocarbons, i.e., naphthenes and paraffins, in an amount up to 30 mass-%. Preferably the isomerizable hydrocarbons consist essentially of aromatics, however, to ensure pure products from downstream recovery processes.

5 According to the present invention, an alkylaromatic hydrocarbon feed mixture, preferably in admixture with hydrogen, is contacted with a catalyst of the type hereinafter described in an alkylaromatic hydrocarbon isomerization zone. Contacting may be effected using the catalyst in a fixed-bed system, a moving-bed system, a fluidized-bed system, or in a batch-type operation. In view of the danger of attrition
10 loss of the valuable catalyst and of the simpler operation, it is preferred to use a fixed-bed system. In this system, a hydrogen-rich gas and the feed mixture are preheated by suitable heating means to the desired reaction temperature and then passed into an isomerization zone containing a fixed bed of catalyst. The conversion zone may be one or more separate reactors with suitable means therebetween to ensure that the
15 desired isomerization temperature is maintained at the entrance to each zone. The reactants may be contacted with the catalyst bed in either upward-, downward-, or radial-flow fashion, and the reactants may be in the liquid phase, a mixed liquid-vapor phase, or a vapor phase when contacted with the catalyst.

 The alkylaromatic feed mixture, preferably a non-equilibrium mixture of C₈
20 aromatics, is contacted with the isomerization catalyst at suitable alkylaromatic-isomerization conditions. Such conditions comprise a temperature ranging from 0° to 600°C or more, and preferably is in the range of from a 300° to 500°C. The pressure generally is from 101.3 to 10130 kPa (1 to 100 atmospheres), preferably less than 5065 kPa (50 atmospheres). Sufficient catalyst is contained in the isomerization zone to
25 provide a liquid hourly space velocity (LHSV) with respect to the hydrocarbon feed mixture of from 0.1 to 30 hr⁻¹, and preferably 0.5 to 10 hr⁻¹. The hydrocarbon feed mixture optimally is reacted in admixture with hydrogen at a hydrogen/hydrocarbon mole ratio of 0.5:1 to about 25:1 or more. Other inert diluents such as nitrogen, argon and light hydrocarbons may be present.

30

The particular scheme employed to recover an isomerized product from the effluent of the reactors of the isomerization zone is not deemed to be critical. Typically, the reactor effluent will be condensed and the hydrogen and light-hydrocarbon components removed therefrom by flash separation. The condensed liquid product then is fractionated to remove light and/or heavy byproducts and obtain the isomerized product. In some instances, certain product species such as ortho-xylene may be recovered from the isomerized product by selective fractionation. The product from isomerization of C₈ aromatics usually is processed to selectively recover the para-xylene isomer either by crystallization or by selective adsorption or by a combination thereof. Selective adsorption is preferred using crystalline aluminosilicates according to US-A-3201491. Improvements and alternatives within the preferred adsorption recovery process are described in US-A-3626020, US-A- 3696107, US-A-4039599, US-A-4184943, US-A-4381419 and US-A-4402832.

In a separation/isomerization process combination relating to the processing of an ethylbenzene/xylene mixture, a fresh C₈-aromatic feed is combined with isomerized product comprising C₈ aromatics and naphthenes from the isomerization reaction zone and fed to a para-xylene separation zone; the para-xylene-depleted stream comprising a non-equilibrium mixture of C₈ aromatics is fed to the isomerization reaction zone, where the C₈-aromatic isomers are isomerized to near-equilibrium levels to obtain the isomerized product. In this process scheme non-recovered C₈-aromatic isomers preferably are recycled to extinction until they are either converted to para-xylene or lost due to side-reactions. Ortho-xylene separation, preferably by fractionation, also may be effected on the fresh C₈-aromatic feed or isomerized product, or both in combination, prior to para-xylene separation.

The type of molecular sieves used in the present invention is within the silicoaluminophosphate molecular sieves described in US-A-4440871. The silicoaluminophosphate molecular sieves are disclosed as microporous crystalline silicoaluminophosphates, having a three-dimensional microporous framework structure of PO₂⁺, AlO₂⁻ and SiO₂ tetrahedral units, and whose essential empirical chemical composition on an anhydrous basis is:



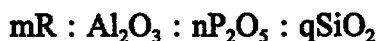
wherein "R" represents at least one organic templating agent present in the intracrystalline pore system; "m" represents the moles of "R" present per mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$ and has a value of from 0.02 to 0.3; "x", "y" and "z" represent, respectively, the mole fractions of silicon, aluminum and phosphorus present in the oxide moiety, said mole fractions being within the compositional area bounded by points A, B, C, D and E on the ternary diagram which is FIG. 1 of US-A-4440871, and represent the following values for "x", "y" and "z":

	<u>Point</u>	<u>Mole Fraction</u>		
		<u>x</u>	<u>y</u>	<u>z</u>
10	A	0.01	0.47	0.52
	B	0.94	0.01	0.05
	C	0.98	0.01	0.01
	D	0.39	0.60	0.01
15	E	0.01	0.60	0.39

The silicoaluminophosphates of US-A-4440871 are generally referred to therein as "SAPO" as a class, or as "SAPO-n" wherein "n" is an integer denoting a particular SAPO such as SAPO-11, SAPO-31, SAPO-40 and SAPO-41. The especially preferred species SAPO-11 as referred to herein is a silicoaluminophosphate having a characteristic X-ray powder diffraction pattern which contains at least the d-spacings set forth below:

<u>SAPO-11</u>			
	<u>2Θ</u>	<u>d</u>	<u>Relative Intensity</u>
5	9.4 - 9.65	9.41 - 9.17	m
	20.3 - 20.6	4.37 - 4.31	m
	21.0 - 21.3	4.23 - 4.17	vs
	21.1 - 22.35	4.02 - 3.99	m
	22.5 - 22.9 (doublet)	3.95 - 3.92	m
	23.15 - 23.35	3.84 - 3.81	ms

10 A modified SAPO-11 is specifically used in the present invention and it is generally known as "SM-3." The composition and properties of SM-3 are specified in the teachings of US-A-4943424. SM-3 comprises a P₂O₅-to-alumina mole ratio at the surface of the silicoaluminophosphate of 0.80 or less, preferably from 0.80 to 0.55; a P₂O₅-to-alumina mole ratio in the bulk of the SAPO of 0.96 or greater, preferably
15 from 0.96 to 1; and a silica-to-alumina mole ratio at the surface which is greater than in the bulk of the SAPO. Preferably the SM-3 has a composition in terms of mole ratios of oxides on an anhydrous basis of:



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system, "m" represents the moles of "R" present and has a value
20 such that there are from 0.02 to 2 moles of "R" per mole of alumina, n has a value of from 0.96 to 1.1 and preferably 0.96 to 1, and q has a value of from 0.1 to 4 and preferably 0.1 to 1. The '424 patent is incorporated herein by reference for its teachings with respect to preparation and properties of the preferred SM-3.

25 The SM-3 sieve preferably is composited with a binder for convenient formation of catalyst particles in a proportion of 5 to 100 mass% SM-3 and 0 to 95 mass-% binder, with the SM-3 preferably comprising from 10 to 90 mass-% of the composite. The binder should be porous, adsorptive support having a surface area of 25 to 500 m²/g, uniform in composition and relatively refractory to the conditions utilized in the

hydrocarbon conversion process. By the term "uniform in composition," it is meant that the support is unlayered, has no concentration gradients of the species inherent to its composition, and is completely homogeneous in composition. Thus, if the support is a mixture of two or more refractory materials, the relative amounts of these materials will be constant and uniform throughout the entire support., It is intended to include within the scope of the present invention carrier materials which have traditionally been utilized in hydrocarbon conversion catalysts such as: (1) refractory inorganic oxides such as alumina, titania, zirconia, chromia, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia, etc.; (2) ceramics, porcelain, bauxite; (3) silica or silica gel, silicon carbide, clays and silicates including those synthetically prepared and naturally occurring, which may or may not be acid treated, for example attapulgite clay, diatomaceous earth, fuller's earth, kaolin, kieselguhr, etc.; (4) crystalline zeolitic aluminosilicates, either naturally occurring or synthetically prepared such as FAU, MEL, MFI, MOR, MTW (IUPAC Commission on Zeolite Nomenclature), in hydrogen form or in a form which has been exchanged with metal cations, (5) spinels such as $MgAl_2O_4$, $FeAl_2O_4$, $ZnAl_2O_4$, $CaAl_2O_4$, and other like compounds having the formula $MO-Al_2O_3$, where M is a metal having a valence of 2; and (6) combinations of materials from one or more of these groups.

The preferred refractory inorganic oxide for use in the present invention is alumina. Suitable alumina materials are the crystalline aluminas known as the gamma, eta-, and theta-alumina, with gamma- or eta-alumina giving best results. A particularly preferred alumina is that which has been characterized in US-A-3852190 and US-A-4012313 as a by-product from a Ziegler higher alcohol synthesis reaction as described in Ziegler's US-A-2892858. For purposes of simplification, such an alumina will be hereinafter referred to as a "Ziegler alumina". Ziegler alumina is presently available from the Vista Chemical Company under the trademark "Catapal" or from Condea Chemie GmbH under the trademark "Pural." This material is an extremely-high-purity pseudoboehmite which, after calcination at a high temperature, has been shown to yield a high purity gamma-alumina.

An alternative preferred binder is a form of amorphous silica. The preferred amorphous silica is a synthetic, white, amorphous silica (silicon dioxide) powder which is classed as wet-process, hydrated silica. This type of silica is produced by a chemical reaction in a water solution, from which it is precipitated as ultra-fine, spherical particles. It is preferred that the BET surface area of the silica is in the range from 120 to 160 m²/g. A low content of sulfate salts is desired, preferably less than 0.3 wt.%. It is especially preferred that the amorphous silica binder be nonacidic, e.g., that the pH of a 5% water suspension be neutral or basic (pH about 7 or above).

A preferred shape for the catalyst composite is an extrudate. The well-known extrusion method initially involves mixing of the non-zeolitic molecular sieve, either before or after adding metallic components, with the binder and a suitable peptizing agent to form a homogeneous dough or thick paste having the correct moisture content to allow for the formation of extrudates with acceptable integrity to withstand direct calcination. Extrudability is determined from an analysis of the moisture content of the dough, with a moisture content in the range of from 30 to 50 wt.% being preferred. The dough then is extruded through a die pierced with multiple holes and the spaghetti-shaped extrudate is cut to form particles in accordance with techniques well known in the art. A multitude of different extrudate shapes are possible, including, but not limited to, cylinders, cloverleaf, dumbbell and symmetrical and asymmetrical polylobates. It is also within the scope of this invention that the extrudates may be further shaped to any desired form, such as spheres, by any means known to the art.

A favored alternative shape of the composite is a sphere, continuously manufactured by the well-known oil drop method. Preferably, this method involves dropping the mixture of molecular sieve, alumina sol, and gelling agent into an oil bath maintained at elevated temperatures. The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. The spheres are then continuously withdrawn from the oil bath and typically subjected to specific aging treatments in oil and an ammoniacal solution to further improve their physical characteristics. The resulting aged and gelled particles are then washed and dried at a relatively low temperature of 50-200°C and subjected to a calcination procedure at a temperature of 450-700°C for

a period of 1 to 20 hours. This treatment effects conversion of the hydrogel to the corresponding alumina matrix.

5 A platinum-group metal, including one or more of platinum, palladium, rhodium, ruthenium, osmium, and iridium, is a preferred component of the present catalyst. The preferred platinum-group metal is platinum. The platinum-group metal component may exist within the final catalyst composite as a compound such as an oxide, sulfide, halide, oxysulfide, etc., or as an elemental metal or in combination with one or more other ingredients of the catalyst composite. It is believed that the best results are obtained when substantially all the platinum-group metal component exists in a reduced state. The platinum-group metal component generally comprises from 0.01 to about 10 2 mass-% of the final catalyst composite, calculated on an elemental basis.

The platinum-group metal component may be incorporated into the catalyst composite in any suitable manner. One method of preparing the catalyst involves the utilization of a water-soluble, decomposable compound of a platinum-group metal to 15 impregnate the calcined sieve/binder composite. Alternatively, a platinum-group metal compound may be added at the time of compositing the sieve component and binder. Yet another method of effecting a suitable metal distribution is by compositing the metal component with the binder prior to co-extruding the sieve and binder. Complexes of platinum-group metals which may be employed according to the above 20 or other known methods include chloroplatinic acid, chloropalladic acid, ammonium chloroplatinate, bromoplatinic acid, platinum trichloride, platinum tetrachloride hydrate, platinum dichlorocarbonyl dichloride, tetramine platonic chloride, dinitrodiaminoplatinum, sodium tetranitroplatinate (II), palladium chloride, palladium nitrate, palladium sulfate, diamminepalladium (II) hydroxide, tetramminepalladium (II) 25 chloride, and the like.

It is within the scope of the present invention that the catalyst composite may contain other metal components known to modify the effect of the platinum-group metal component. Such metal modifiers may include rhenium, tin, germanium, lead, cobalt, nickel, indium, gallium, zinc, uranium, dysprosium, thallium, and mixtures thereof. Catalytically effective amounts of such metal modifiers may be incorporated 30

into the catalyst by any means known in the art to effect a homogeneous or stratified distribution.

5 The catalyst composite of the present invention may contain a halogen component. The halogen component may be either fluorine, chlorine, bromine or iodine or mixtures thereof, with chlorine being preferred. The halogen component is generally present in a combined state with the inorganic-oxide support. The optional halogen component is preferably well dispersed throughout the catalyst and may comprise from more than 0.2 to 15 wt.%, calculated on an elemental basis, of the final catalyst. The halogen component may be incorporated in the catalyst composite in any
10 suitable manner, either during the preparation of the inorganic-oxide support or before, while or after other catalytic components are incorporated.

 The catalyst composite is dried at a temperature of from 100° to 320°C for a period of from 2 to 24 or more hours and, usually, calcined at a temperature of from 400° to 650°C in an air atmosphere for a period of from 0.1 to 10 hours until the
15 metallic compounds present are converted substantially to the oxide form. If desired, the optional halogen component may be adjusted by including a halogen or halogen-containing compound in the air atmosphere.

 The resultant calcined composite optimally is subjected to a substantially water-free reduction step to insure a uniform and finely divided dispersion of the optional
20 metallic components. The reduction optionally may be effected in the process equipment of the present invention. Substantially pure and dry hydrogen (i.e., less than 20 vol. ppm H₂O) preferably is used as the reducing agent in this step. The reducing agent contacts the catalyst at conditions, including a temperature of from 200° to 650°C and for a period of from 0.5 to 10 hours, effective to reduce substantially all of the
25 Group VIII metal component to the metallic state. In some cases the resulting reduced catalyst composite may also be beneficially subjected to presulfiding by a method known in the art to incorporate in the catalyst composite from 0.05 to 0.5 mass-% sulfur calculated on an elemental basis.

EXAMPLES

Samples of SM-3 modified silicoaluminophosphate were prepared for testing as isomerization catalysts in the process of the invention. The SM-3 was prepared according to the teachings of US-A-4943424 and had characteristics as disclosed in the '424 patent.

Samples of unmodified SAPO-11 silicoaluminophosphate not of the invention were prepared in accordance with the teachings of US-A-4440871 and as described hereunder. Molar proportions of 50 moles water to 1.8 moles of orthophosphoric acid as 85 mass-% H_3PO_4 were combined, and 1.0 moles of alumina was added to the solution as Versal 250 with stirring of the mixture. Silica then was added as HiSil 250 in a molar proportion of 0.2 moles. The directing agent was di-n-propylamine, added in a proportion of 1.8 moles. The composition of the reaction mixtures therefore was as follows:



SAPO-11 seed amounting to 1.0 mass-% of the oxides was added and the reaction mixture was heated gradually to 195°C and held at that temperature for 12 hours. The solid reaction product was recovered by centrifugation, washed with water and dried in air at 100°C. Certain of the synthesis powders were bound with alumina as described below and then were calcined at 650° C. in flowing air to remove the synthesis template and set the silica binder of the bound catalyst samples. The unbound control SAPO-11, not of the invention, was designated as "Control."

Example I

The advantage of the process of the invention was demonstrated in a series of microreactor tests. Unbound catalysts were loaded in the microreactor in a quantity of 250 mg. Meta-xylene was fed to the reactor in a hydrogen atmosphere at varying temperatures. Conversion of the meta-xylene was measured, as well as the ratio of para-xylene to ortho-xylene in the product. The test results showed the following for

the SM-3 silicoaluminophosphate in comparison to the control SAPO-11 not of the invention:

		<u>400°C</u>		<u>500°C</u>	
		<u>SM-3</u>	<u>Control</u>	<u>SM-3</u>	<u>Control</u>
5	Conversion, %	39.14	3.27	47.44	9.2
	P-x/o-x, mole-%	1.24	0.73	1.06	1.6

The SM-3 showed a substantial advantage over the control catalyst in meta-xylene conversion at both temperatures. SM-3 also showed control of the para-xylene/ortho-xylene ratio near equilibrium ratios, while ratios of the xylene isomers varied sharply at the low conversion provided by the control catalyst.

Example II

The SM-3 silicoaluminophosphate was composited with alumina and tetramine platinic chloride at alternative platinum levels to aid in formulating the optimum catalyst of the invention. The composites comprised 60 mass-% SM-3 and 40 mass-% alumina. Tetramine platinic chloride was incorporated into the composites to effect platinum contents of 0.28 and 0.14 mass-%, respectively, on an elemental basis, and the catalysts were calcined and reduced.

The catalysts were evaluated using a pilot plant flow reactor processing a non-equilibrium C₈-aromatic feed having the following composition in mass-%:

20	ethylbenzene	17%
	meta-xylene	58%
	ortho-xylene	25%

This feed was contacted with 100 cc of catalyst at a LHSV of 2 hr⁻¹, and a hydrogen/hydrocarbon mole ratio of 4. Reactor temperature was adjusted to effect a favorable conversion level. Conversion is expressed as the disappearance per pass of ethylbenzene. C₈-aromatic loss is primarily to benzene and toluene, with smaller amounts of light gases being produced. Results were as follows:

<u>Catalyst mass-% Pt</u>	<u>0.28</u>	<u>0.14</u>
Temperature, °C	386	380
Ethylbenzene conversion, %	28	24.5
C ₈ -aromatics loss, %	2.8	2.8

5 Example III

Catalyst samples were prepared and tested to illustrate the effect of platinum location on the performance of the catalyst. Catalyst A was prepared as in Example II by coextruding SM-3 silicoaluminophosphate and alumina in a 60/40 mass ratio with tetramine platinum chloride, calcining and reducing to effect a catalyst containing 0.28 mass-% platinum. Catalyst B was prepared by first compositing alumina and tetramine platinum chloride, followed by coextruding with SM-3, calcining and reducing to effect a catalyst having the same overall composition as Catalyst A.

The catalysts were evaluated using a pilot plant flow reactor processing the same non-equilibrium C₈-aromatic feed as in Example II. This feed was contacted with 100 cc of catalyst at a LHSV of 2 hr⁻¹ and a hydrogen/hydrocarbon mole ratio of 4. Reactor temperature was adjusted to effect a favorable conversion level. Conversion is expressed as the disappearance per pass of ethylbenzene, and C₈-aromatic loss is primarily to benzene and toluene. Results were as follows:

<u>Catalyst:</u>	<u>A</u>	<u>B</u>
Temperature, °C	386	386
Ethylbenzene conversion, %	28	27.5
C ₈ -aromatics loss, %	2.8	2.7



CLAIMS:

- 5 1. A process for the isomerization of a non-equilibrium feed mixture of xylenes and ethylbenzene comprising contacting the feed mixture in the presence of hydrogen in an isomerization zone with a catalyst composite comprising an effective amount of an SM-3 crystalline silicoaluminophosphate molecular sieve at C₈ isomerization conditions effective to obtain an isomerized product comprising a higher proportion of p-xylene than in the feed mixture.
2. The process of Claim 1 wherein the catalytic composite comprises an effective amount of a platinum-group metal component.
- 10 3. The process of Claim 1 or 2 wherein the catalyst composite further comprises an inorganic-oxide binder comprising alumina and silica or a mixture thereof.
4. The process of Claim 2 wherein the effective amount of a platinum-group metal component comprises from 0.1 to 5 mass-% platinum on an elemental basis.
- 15 5. The process of any one of Claims 1 to 4 wherein the isomerized product comprises a greater-than-equilibrium concentration of para-xylene.
6. The process of any one of Claims 1 to 5 wherein the catalyst composite comprises from 0.1 to 5 mass-% on an elemental basis of a platinum component, from 10 to 100 mass-% of an SM-3 crystalline silicoaluminophosphate molecular sieve and an inorganic-oxide binder.
- 20 7. The process of any one of Claims 1 to 6 wherein the C₈ aromatic isomerization conditions include comprising a temperature of from 300° to 500°C, a pressure of from 101.3 to 5065 kPa (1 to 50 atm), a LHSV from 0.5 to 10 hr⁻¹ and a hydrogen-to-hydrocarbon mole ratio of from 0.5:1 to 25:1.
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**"C₈ AROMATICS ISOMERIZATION USING CATALYST CONTAINING
MODIFIED SILICOALUMINOPHOSPHATE MOLECULAR SIEVE"**

5

ABSTRACT

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A non-equilibrium C₈ aromatic-feed mixture is selectively isomerized to obtain an isomerized product enriched in para-xylene by contacting the feed in the presence of hydrogen with a catalyst containing a combination of a platinum group component with an SM-3 acidic crystalline silicaaluminophosphate molecular sieve at C₈ aromatic isomerization conditions. The SM-3 molecular sieve is enriched in framework silicon at the surface, resulting in a greater yield of para-xylene compared to prior art processes.