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(54) Title: DIRECT PARAFFIN AND AROMATIC ALKYLATION AND PARAFFIN ISOMERIZATION

(57) Abstract

A process is provided for direct aromatics alkylation with alkanes by contacting a hydrocarbon feed containing an aromatic hydrocarbon and an alkane having at least 15 carbon atoms with a molecular sieve catalyst which includes incorporated metal. Alkane isomerization can occur concurrently with the aromatics alkylation.

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DIRECT PARAFFIN AND AROMATIC ALKYLATION AND PARAFFIN ISOMERIZATION

The invention relates to the direct alkylation of aromatic hydrocarbons with paraffins to produce linear alkylbenzenes, lubricant base stocks or chemical intermediates.

In conventional processes to produce alkylaromatics, an aromatic hydrocarbon is alkylated with a reactive agent such as olefin, alkyl halide or alkyl alcohol, in a Friedel-Crafts type reaction. Processes of this type are described, e.g., in U.S. Patent Nos. 3,755,483 to Burress, 4,301,316 and 4,301,317 to Young, 4,871,444 to Chen et al. and 4,990,718 to Pelrine. U.S. Patent No. 3,755,483 utilizes zeolites in the hydrogen form. U.S. Patent Nos. 4,301,316 and 4,301,317 describe Friedel-Crafts type reactions over certain zeolites in which cationic sites are associated with metals including rare earth, zinc, copper or aluminum. U.S. Patent No. 4,871,444 utilizes rare earth exchanged zeolite. U.S. Patent No. 4,990,718 describes utilizing a Group VIB metal oxide such as chromium oxide to produce olefin dimers, followed by Friedel-Crafts type aromatics alkylation over zeolites in the ammonium form. In addition, U.S. Patent No. 4,358,628 describes benzene alkylation with detergent range olefins over tungsten oxide on silica-alumina.

Unfunctionalized paraffins have, however, generaly been considered to be inactive in alkylating aromatics under Friedel-Crafts conditions. A review article by P. R. Pujadó entitled "Linear Alkylbenzene (LAB) Manufacture", *Handbook of Petroleum Processes,* 2nd Ed. Robert Meyers, Ed., McGraw-Hill, New York, 1996, pages 1.53-1.66, describes alkylation of benzene with olefins or alkyl chlorides. The article avers that, to date, attempts to alkylate n-paraffin with benzene directly have failed.

U.S. Patent No. 4,524,230 to Haensel describes an indirect aromatics alkylation which involves decomposing a paraffinic hydrocarbon on the surface of a nonacid-active catalyst which includes nickel, cobalt, or iron on a non-acid-acting support such as kieselguhr, silica or neutralized zeolite. Paraffins are fragmented and the fragments scavenged by an aromatic compound. Because of the fragmentation, the product alkylaromatic always contains an alkyl group which has fewer carbons than the paraffin feed.

Lube base stocks are conventionally obtained from the refining of petroleum through a series of operations which remove unwanted components. These operations are directed towards obtaining a lubricant base stock of suitable boiling point, viscosity, viscosity index and other characteristics.

Lubricants should be highly paraffinic since paraffins possess the desirable combination of low viscosity and high viscosity index. Waxy n-paraffins and slightly branched paraffins, e.g., n-methyl paraffins, however, are waxy materials which confer an unacceptably high pour point on the lubricant base stock and are therefore catalytically dewaxed or removed during solvent dewaxing operations. Less waxy isoparaffins have relatively high viscosity index with low pour point properties.

Hydroisomerization of waxy n-paraffins over platinum-containing, highly siliceous zeolite beta is described in U.S. Patent Nos. 4,419,220 and 4,518,485 to La Pierre et al. During isomerization, the waxy components are converted to relatively less waxy isoparaffins and at the same time, the slightly branched chain paraffins undergo isomerization to more highly branched aliphatics. A measure of cracking can take place during the operation so that not only is the pour point reduced by reason of the isomerization but, in addition, the heavy ends undergo some cracking or hydrocracking to form liquid range materials which can contribute to a low viscosity product. The degree of cracking, however, is limited so as to maintain as much of the feedstock as possible in the desired boiling range.

According to the present invention, it has now been found that alkylaromatic compounds useful in the production of detergents, as precursors for plastics and as lubricating oil base stocks can be produced by direct aromatic alkylation with paraffins, optionally with concurrent paraffin isomerization, by contacting a hydrocarbon feed containing aromatics and C_{15}+ alkanes with a metal-containing molecular sieve catalyst under aromatics alkylation conditions. Alkanes are used directly as the alkylating agent for aromatics and at the same time, alkanes may be isomerized. As used herein, the phrase “direct alkylation” means a process where the paraffin, which is usually inactive under prior art Friedel-Crafts reaction conditions, is used directly as an alkylating agent without the need for functionalizing the paraffin.

Thus, in its broadest aspect the invention resides a process for direct alkylation of an aromatic hydrocarbon with an alkane comprising contacting a feed comprising an aromatic hydrocarbon and an alkane having at least 15 carbon atoms with a catalyst comprising a molecular sieve material having an incorporated metal component.

Preferably, the molecular sieve catalyst has a pore/channel channel system having openings of 10 or more oxygen ring members. The preferred metal component is selected from Groups VIA, VIIA and VIIIA of the Periodic Table of the Elements (IUPAC version), and most preferably is a noble metal.

The invention provides an efficient way to produce alkylaromatics which bypasses the use of the more expensive olefins or functionalized paraffins that are required in Friedel-Crafts type reactions. Therefore alkylation of aromatics with alkanes takes place in the absence of the addition of functionalized alkanes such as olefins, alkyl halides or alkyl alcohols. Aromatics can be reacted directly with paraffins without significant paraffin cracking.

Furthermore, when applied to lubricant base stock production, by adjusting reaction conditions and catalysts such that the alkylaromatics produced have desirable lubricant properties, the process not only isomerizes linear paraffins but also adds aromatic components into the product. This way of incorporating aromatics provides lubricant base stocks with better pour point, better low temperature viscometric properties, and better additive solubility than catalytically or solvent dewaxed lubricant base stock.

FEED

The aromatic component of the feed to the process can be any mononuclear or polynuclear aromatic hydrocarbon. These feeds can be available from petroleum, coal or synthetic fuel or byproducts from chemical processing. Suitable aromatic hydrocarbons include, for example, benzene, naphthalene, anthracene and their alkylated analogs, such as methylated or ethylated benzenes or napthalenes, etc. Preferred aromatics for the feed include benzene and naphthalene.

The alkane component of the feed to the process comprises at last one paraffinic hydrocarbon having at least 15 carbon atoms and may range from a linear or very slightly branched paraffin having from 15 to 22 carbon atoms, to light, medium or heavy slack wax, paraffinic FCC bottoms, deasphalted hydrocracked bottoms, Fischer-Tropsch synthetic distillate and wax, deoiled wax or polyethylene wax, light or heavy cycle oil. Other sources include waxy shale oil, tar sands and synthetic fuels. Lower molecular weight paraffins may also be present in the alkane component of the feed.

Slack waxes are generally described in U.S. Patent Nos. 5,110,445 to Chen and Partridge and 5,208,403 to Buchanan and Wu. Highly paraffinic streams such as those obtained from the solvent dewaxing of distillates and other lube fractions are commonly referred to as slack wax. These highly paraffinic streams, comprising mostly straight chain and mono-methyl paraffins, generally have a paraffin content of at least 50 wt. percent, more usually at least 70 wt. percent or above, with the balance from the occluded oil being divided between aromatics and naphthenics. These waxy, highly paraffinic stocks usually have much lower viscosities than vacuum distilled neutral or residual stocks because of their relatively low content of aromatics and naphthenes which are high viscosity components. Slack waxes are obtained, for example, as the waxy product obtained directly from a solvent dewaxing process, e.g., an MEK or propane dewaxing process.

Fischer-Tropsch wax is another preferred feed. Fischer-Tropsch synthesis involves the catalytic hydrogenation of carbon monoxide. Fischer-Tropsch liquid obtained, e.g., with cobalt-containing catalysts, is roughly equivalent to a very paraffinic sulfur free natural petroleum oil. Straight-chain, saturated aliphatic molecules predominate.

The molar ratio of aromatics to paraffins in the feed useful herein may vary from 0.1 to 30. The preferred molar feed ratio of aromatics to paraffins varies from 1.5 to 10. If the feeds are benzene and hexadecane, for example, the preferred feed composition will contain 34 wt.% to 78 wt.% benzene. If the feeds are benzene and heavy neutral slack wax (with average molecular weight of 492), the preferred feed composition will contain 19 wt.% to 61 wt.% benzene.

The feeds contain paraffins in an amount of at least 5 weight percent (wt.%), preferably at least 20 wt.%, more preferably 50 wt.% and higher. More particularly, the feeds contain paraffins in an amount preferably greater than 10 mole percent (mole.%), more preferably, 20-80 mole.%, and most preferably, 40-60 mole.% consistent with the amount of aromatics.

CATALYSTS

The catalysts of the present invention are bifunctional in character, comprising a metal hydrogenation-dehydrogenation component on a molecular sieve which supplies an acidic functionality. The catalysts of the present invention include as non-limiting examples, ZSM-5 (U.S. Pat. No. 3,702,886 and Re. 29,948), mordenite, ZSM-12 (U.S. Pat. No. 3,832,449), ZSM-23 (U.S. Pat. No. 4,076,842), ZSM-48 (U.S. Pat. No. 4,397,827), Zeolite Beta (U.S. Pat. Nos. 3,308,069 and Re. 28,341), USY (U.S. Pat. Nos, 3,293,192 and 3,449,070), MCM-

22 (U.S. Pat. No. 4,954,325), MCM-36 (U.S. Pat. No. 5,229,341), MCM-49 (U.S. Pat. No. 5,236,575), and MCM-56 (U.S. Pat. No. 5,362,697) and mesoporous materials such as M41S (U.S. Pat. No. 5,102,643) and MCM-41 (U.S. Pat. No. 5,098,684).

The catalysts are incorporated with a metal having a strong hydrogenation function, particularly noble metals and other metals from Groups VIA, VIIA and VIIIA of the Periodic Table of the Elements (IUPAC Version) including chromium, molybdenum, tungsten, manganese, technitium, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, gold, silver, zinc and cadmium; especially platinum, palladium, rhenium, rhodium, iridium, and combinations thereof; and preferably platinum or palladium. The metal component can be incorporated by methods known in the art, e.g., by impregnation or cation exchange, usually in amounts of from 0.01 to 10 wt.% of the total catalyst and preferably from 0.1 to 2.0 wt.% of the catalyst.

A metal stabilizer or promoter, such as tin, indium, gallium, thorium or lead, e.g., in an amount of 0.01 wt.% to 10 wt.% of the catalyst, may also be added to the system, such as is described in U.S. Patent No. 5,012,021.

The crystalline molecular sieve may also be composited with a matrix material, including synthetic and naturally occurring substances, e.g., clay, silica, alumina, zirconia, titania, silica-alumina and other metal oxides. Naturally-occurring clays include those of the montmorillonite and kaolin families. The matrix itself may possess catalytic properties, often of an acid nature. Other porous matrix materials include 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-alumina-zirconia. A mixture of these components can also be used. The relative proportions of crystalline molecular sieve material and matrix may vary widely from 1 to 90 wt.%, usually 20 to 80 wt.%. The catalyst can also be used in the absence of matrix or binder, i.e., in unbound form. The catalyst can be used in the form of an extrudate, lobed form (e.g. trilobe), or powder.

The catalyst is usually pretreated with flowing H_2 at 100-500°C, H_2 flow rate of 1-1000 cc/min., pressure of atm.-500 psi for 1 min. to 16 hrs. The catalyst can be regenerated by treating with H_2 at high temperature, e.g., over 350°C, H_2 flow rate of 1-1000 cc/min., pressure of atm.-500 psi for 1 min. to 16 hrs.; or the catalyst can be regenerated by air or oxygen calcination at over 350°C for 0.5 to 24 hrs., followed by H_2 pretreatment as described above.

PROCESS CONDITIONS

In general, the process is operated under conditions including an elevated temperature preferably ranging from 100°C or 150°C to 400°C (212°F or 302°F to 752°F), more preferably 200°C to 350°C (392°F to 662°F), most preferably 200°C to 300°C (392°F to 572°F); a pressure preferably ranging from atmospheric to 2500 psig, more preferably 200 to 2000 psig, and most preferably 300 to 1500 psig; a space velocity preferably ranging from 0.01 to 100 LHSV, more preferably 0.1 to 50 LHSV, and most preferably 0.1 to 10 LHSV; a molar feed ratio of aromatics/paraffins preferably ranging from 0.1 to 30, more preferably 0.5 to 15, and most preferably 1.5 to 10. Hydrogen may be used but is not required, and the process is preferably carried out in the absence of added hydrogen. Conditions may be adjusted toward aromatics alkylation or toward paraffin isomerization. This can be accomplished by selecting the catalyst or reaction conditions. For example, some catalysts, e.g., ZSM-5, ZSM-12, ZSM-23, mordenite or ZSM-48, promote more isomerization, whereas other catalysts, e.g., MCM-22 type, zeolite beta, M41S, and USY, promote more alkylation.

The process can be carried out in several different types of reactors, e.g., fixed-bed continuous flow, batch, continuous stir tank, or bubble-column type reactors.

PRODUCTS

A notable feature of the present process is that the aromatic is alkylated with a paraffin with various degrees of isomerization to produce linear alkylaromatics, branched alkylaromatics and iso-paraffins. The useful products include chemical intermediates such as polymer precursors, high-quality lubricant base stocks and detergent precursors.

When using slack wax, FT wax or hydrocracked bottoms as paraffin feed, the lubricant base stock products contain alkylated aromatics and isomerized paraffins. These components enhance the quality of a lubricant base stock offering advantages of feedstock flexibility, better pour point and low-temperature viscometric properties and better additive solubility. Therefore, the lubricant base stock products have desirable properties of pour point, viscosity and viscosity index. Pour point is the lowest temperature at which a petroleum oil will flow or pour when it is chilled without disturbance at a controlled rate. Pour point is a critical specification of lubricant oils used in cold climates. Viscosity is the property of liquids under flow conditions which causes the oil to resist instantaneous change of shape or rearrangement of their ports due to internal friction. Viscosity is generally measured as the number of seconds, at a definite temperature, required for a standard quantity of oil to flow through a standard apparatus. Common viscosity scales are Saybolt Universal (SU), Saybolt Fural, and Kinematic (Stokes). The Viscosity Index (V.I.) is a quality parameter of lubricating oils which indicates the rate of change of viscosity with change in the temperature. The higher the V.I., the smaller its change in viscosity for a given change in temperature. A high V.I. indicates an oil that does not tend to become viscous at low temperature or become thin at high temperatures. The process of the invention produces lubricant base stock with high V.I., low pour point, and additive solubility suitable for high performance lubricant product formulation.

When using long-chain paraffins such as C_{15} to C_{22}, preferably C_{15} to C_{18}, the corresponding alkylaromatics useful as detergent alkylates can be produced, preferably over metal-containing MCM-22 type catalysts, particularly Pt/MCM-22. Detergent alkylate generally includes mostly linear alkylbenzenes which are later sulfonated to yield detergent. Detergents are commonly anionic surfactants which include linear sodium alkyl benzene sulfonate (LAS), linear alkyl sulfates, and linear alkyl ethoxy sulfates. The biodegradability of alkylbenzenesulfonic acid based detergents is enhanced when the average substituent position of the benzene ring on the alkyl chain is lower, e.g., a detergent based on (2-alkyl)benzenesulfonic acid is more easily biodegraded than one based on (3-alkyl)benzenesulfonic acid, etc. The higher content of 2-phenyl-alkane also improves the solubility of the sulfonated linear alkylbenzenes. The alkylbenzenes produced over metal-containing MCM-22 type catalysts in the invention contain, e.g., 40% of 2-alkyl benzene and 96% or more of linear alkylbenzenes.

The following non-limiting examples illustrate the invention.

EXAMPLE 1

Pt-free zeolite beta/35% Al_2O_3 as 1/20" quadrulobe (9 alpha).

65 parts of zeolite beta and 35 parts LaRoche Versal alumina was extruded into a 1/20" quadrulobe shape. (Shaped extrudates are described, e.g., in U.S. Patent No. 4,441,990 to Huang). After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. After calcination, the extrudate was steamed to an alpha activity of 9.

EXAMPLE 2

0.6% Pt/zeolite beta/35% Al_2O_3 as 1/20" quadrulobe (9 alpha).

The steamed extrudate of Example 1 (alpha = 9) was exchanged with platinum tetraammine chloride and ammonium nitrate (competitive exchange) to a concentration of 0.6 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 360°C.

EXAMPLE 3

0.6%Pt/[B] zeolite beta/35% SiO_2 as 1/20" quadrulobe.

65 parts of boron containing zeolite beta and 35 parts LaRoche Versal alumina was extruded into a 1/20" quadrulobe shape. After drying at 121° C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. The alpha activity of the calcined extrudate was 7. After calcination, the extrudate was exchanged with platinum tetraammine chloride and ammonium nitrate (competitive exchange) to a concentration of 0.6 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 360°C.

EXAMPLE 4

0.6% Pt/zeolite beta/35% Al_2O_3 as 1/16" quadrulobe (50 alpha).

65 parts of zeolite beta and 35 parts LaRoche Versal alumina was extruded into a 1/20" quadrulobe shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. After calcination, the extrudate was steamed to an alpha activity of 50. After steaming, the extrudate was exchanged with platinum tetraammine chloride to a concentration of 0.6 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 360°C.

EXAMPLE 5

0.7% Pt/USY/35% Al_2O_3 as 1/16" quadrulobe.

65 parts of USY (Tosoh 360HUA) and 35 parts LaRoche Versal alumina was extruded into a 1/20" quadrulobe shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. The extrudate was exchanged with platinum tetraammine chloride and ammonium nitrate (competitive exchange) to a concentration of 0.6 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 360°C.

EXAMPLE 6

0.6% Pt/MCM-22 as 1/16" extrudate.

100 parts of MCM-22 was extruded into a 1/16" cylindrical shape. After drying at 121°C, the binderless MCM-22 extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the binderless extrudate was calcined in nitrogen at 482°C for 3 hours followed by calcination in air at 538°C for 12 hours. After calcination, the binderless extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 7

0.6% Pt/MCM-22/35% Al_2O_3 as 1/16" extrudate.

65 parts of MCM-22 and 35 parts LaRoche Versal alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. This calcined catalyst had an alpha value of 280. After calcination, the alumina bound extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 8

0.6% Pt/MCM-49/35% Al_2O_3 as 1/16" quadrulobe.

65 parts of MCM-49 and 35 parts LaRoche Versal alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. After calcination, the alumina bound extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 9

0.6% Pt/MCM-56/35% Al_2O_3 as 1/16" quadrulobe.

65 parts of MCM-56 and 35 parts LaRoche Versal alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. After calcination, the alumina bound extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360° C.

EXAMPLE 10

0.5% Pt/ZSM-12 as 1/16" extrudate.

100 parts of ZSM-12 was extruded with sodium hydroxide into a 1/16" cylindrical shape. After drying at 121°C, the binderless ZSM-12 extrudate was exchanged with ammonium nitrate to remove sodium. After rinsing with deionized water to remove residual nitrate, the binderless extrudate was calcined in nitrogen at 482°C for 3 hours followed by calcination in air at 538°C for 12 hours. This zeolite was steamed to an alpha of 1. After calcination, the binderless extrudate was impregnated with 0.5 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 11

0.6% Pt/ZSM-12/35% Al_2O_3 as 1/16" extrudate.

65 parts of ZSM-12 and 35 parts SB alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by calcination in air at 538°C. After calcination, the alumina bound extrudate was ion exchanged with ammonium nitrate to remove residual sodium. After drying at 121° C, the sodium-free extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 12

0.4% Pt/ZSM-5/35% Al_2O_3 as 1/16" extrudate.

65 parts of ZSM-5 and 35 parts LaRoche Versal alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. After calcination, the alumina bound extrudate was steamed to an alpha activity of 1. After steaming, the ZSM-5 extrudate was ion exchanged with platinum tetraammine chloride to 0.6 wt.% Pt. After exchange, the extrudate was washed with deionized water to remove any residual nitrates followed by drying at 121°C. After drying at 121°C, the platinum containing extrudate was calcined in air at 371°C.

EXAMPLE 13

0.6% Pt/ZSM-23/35% Al_2O_3 as 1/16" extrudate.

65 parts of ZSM-23 and 35 parts Condea SB alumina was extruded into a 1/16" cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After sodium removal, the extrudate was exchanged with platinum tetraammine chloride and ammonium nitrate (competitive exchange) to a concentration of 0.5 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 377°C.

EXAMPLE 14

0.6% Pt/Mordenite/35% Al_2O_3 as 1/16” extrudate.

65 parts of TEA Mordenite and 35 parts LaRoche Versal alumina was extruded into a 1/16” cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. After calcination, the alumina bound extrudate was impregnated with 0.6 wt.% Pt using platinum tetraammine nitrate salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 15

0.5% M41S (80 Å)/35% Al_2O_3 as 1/16” extrudate.

65 parts of M41S (pore diameter 80 Å) and 35 parts LaRoche Versal alumina was extruded into a 1/16” cylindrical shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C. The extrudate was exchanged with ammonium nitrate to remove any exchangeable sodium. After rinsing with deionized water to remove residual nitrate, the extrudate was calcined in air at 538°C. After calcination, the alumina bound extrudate was impregnated with 0.5 wt.% Pt using platinum tetraammine chloride salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 16

0.6% Pt/zeolite beta/35% Al_2O_3 as 1/16” extrudate.

65 parts of zeolite beta and 35 parts LaRoche Versal alumina was extruded into a 1/20” quadrulobe shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by air calcination at 538°C. After calcination, the extrudate was steamed to an alpha activity of 17. The steamed extrudate was exchanged with platinum tetraammine chloride to a concentration of 0.6 wt.% Pt metal. After ion exchange, the extrudate was washed with deionized water to remove chlorides and dried at 121°C. After drying, the extrudate was calcined in air at 360°C.

EXAMPLE 17

1.0% Pt/Sn/ZSM-5/35% Al_2O_3 as 5/32" trilobe.

65 parts of Sn ZSM-5 and 35 parts LaRoche Versal alumina was pelleted into a 5/32" trilobe shape. After drying at 121°C, the extrudate was calcined in nitrogen at 482°C followed by calcination in air at 538°C. After calcination, the alumina bound extrudate was impregnated with 1.0 wt.% Pt using platinum tetraammine hydroxide salt. After drying at 121°C, the platinum containing extrudate was calcined in air at 360°C.

EXAMPLE 18

Fixed-Bed Catalyst Screening Using n-Hexadecane and Benzene

Molecular sieve catalysts as prepared in Examples 1 to 14 were tested for n-hexadecane/benzene reaction in fixed-bed reactors. The following general procedures were used for the fixed-bed experiments.

The catalyst (extrudate or quadrulobe) was broken into pieces about 1/8" long. The catalyst screening test was carried out in a down-flow fixed-bed reactor in the liquid phase. The reactor was heated with a 3-zone furnace. The catalyst bed (5, 10, or 15 cc of catalyst diluted with sand) was located in the mid-zone. Top and bottom portions of the reactor were filled with sand. For each test, the catalyst was pretreated with 100-200 cc/min flowing hydrogen for 2 hr at 350°C and ambient pressure. Hydrogen was turned off and the reactor temperature was reduced to desired reaction temperature ranging from 210°C to 300°C depending on catalyst activity. The reactor pressure was set to 750 psig with a grove loader. Feed (benzene alone or as a 6:1 benzene/n-hexadecane molar ratio mixture) was introduced to the reactor at 60 cc/hr for 1 hr. After reaching the desired pressure, benzene and n-hexadecane were fed in a 6:1 molar ratio with n-hexadecane flow rate adjusted between 0.1 to 0.3 LHSV based on total catalyst volume. After lineout, the reactor effluent was collected in a cold trap and analyzed with an off-line GC. Catalyst results are summarized in Example 19.

EXAMPLE 19

Fixed-Bed Test Results for n-Hexadecane and Benzene Reaction

Representative data of fixed-bed n-hexadecane and benzene reaction at 750 psig and 6:1 benzene/n-hexadecane molar ratio using catalysts as prepared in Examples 1 to 14 are shown in Tables 6 to 9 below. Zeolite beta and USY catalysts are shown in Table 6, MCM-22 type catalysts in Table 7, ZSM-12 catalysts in Table 8, and ZSM-5, ZSM-23, and mordenite catalysts are in Table 9. One representative reaction condition for each catalyst is given along with observed n-hexadecane conversion, benzene conversions, n-hexadecane utilization, and benzene utilization. n-Hexadecane utilization and benzene utilization are defined below:

n-Hexadecane utilization

= 100% x (wt. of n-hexadecane converted into a given product or products)/overall wt. of n-C_{16} converted

Benzene utilization

= 100% x (wt. of benzene converted into a given product or products)/overall wt. of benzene converted

For light alkylbenzenes, it is assumed that the alkyl groups are originated from n-hexadacane and the phenyl group is originated from benzene.

Data in Table 1 below shows that when using a Pt-free zeolite beta (catalyst prepared in Example 1), only ~1% n-hexadecane conversion was observed at 300°C. The same zeolite beta catalyst with 0.6% Pt (catalyst prepared in Example 2) converted 28% n-hexadecane at 250°C with 24% n-hexadecane utilization for iso-hexadecane and 52% for phenylhexadacane. This comparison indicated that metal such as noble metal Pt is important for the desired isomerization and alkylation to occur.

The data with the Pt/zeolite beta catalysts (prepared in Examples 2 and 4) indicated that zeolite beta with alpha value ranging from 7 to 50 are both active for paraffin alkylation with concurrent paraffin isomerization.

Pt/zeolite beta and Pt/USY catalyzed n-hexadecane isomerization and n-hexadecane/benzene alkylation simultaneously. The hexadecylbenzene products produced from these catalysts consisted 39-81% of linear hexadecylbenzenes (8-16% being 2-phenylhexadecane), and the balance of the hexadecylbenzene products was branched hexadecylbenzenes (19-61%). Pt/zeolite beta and Pt/USY can be used for simultaneous paraffins isomerization and paraffin/aromatics alkylation where alkylation is the main reaction. These catalysts can also be used for incorporation of aromatic hydrocarbons into linear and branched paraffins during lube dewax process.

Table 1

Fixed-Bed Test Results with Zeolite Beta and USY[a]

Catalyst prepared in	Example 1	Example 2	Example 3	Example 4	Example 5
Catalyst	Pt-free Zeolite Beta	0.6% Pt Zeolite Beta	0.6% Pt [B] Zeolite Beta	0.6% Pt Zeolite Beta	0.7% Pt USY
Temp., °C	299	250	250	232	251
n-C_{16} LHSV, h^{-1}	0.30	0.30	0.30	0.15	0.15
Days on stream	10.0	11.0	5.0	12.0	6.8
n-C_{16} Conv, %	~1.0	28.0	16.5	21.7	28.7
Benz. Conv, %	~0	6.6	3.8	6.4	10.4
n-C_{16} utilization, %					
Light paraffins & light alkylbenzenes	-	22.3	32.4	35.9	16.8
Iso-C_{16}	-	24.0	17.6	11.5	18.5
C_{16}-Bz	-	52.2	50.1	52.4	55.0
Others[b]	-	1.5	0.0	0.2	9.7
Benzene utilization, %					
c-C_6 and c-C_{12}[c]	-	35.4	26.4	19.8	56.7
Light alkylbenzenes	-	24.5	38.1	44.0	11.6
C_{16}-Bz	-	36.9	33.3	34.4	26.8
Others[b]	-	3.2	2.2	1.8	4.8
Hexadecylbenzene ratio, % (L-C_{16}-Bz: linear hexadecylbenzene)					
2-Bz-C_{16}/all C_{16}-Bz	-	16	13	8	16
L-C_{16}-Bz/all C_{16}-Bz	-	57	52	39	81

[a] 750 psig, 6:1 benzene/n-hexadecane molar ratio. Bz is benzene.

[b] C_{12}-tetralins, C_{13}-indanes, C_{12}-naphthalenes, and traces of diphenyl hexadecanes were detected.

[c] From benzene hydrogenation and hydrodimerization with hydrogen generated during n-hexadecane/benzene alkylation.

Data in Table 2 below show that both alumina-bound and binder-free Pt/MCM-22 were very active for n-hexadecane alkylation with aromatics and/or isomerization. The hexadecylbenzene products produced from alumina-bound Pt/MCM-22, Pt/MCM-49, and

Pt/MCM-56 consisted of 96-97% linear hexadecylbenzenes (37-43% being 2-phenylhexadecane). These catalysts can therefore be applied for linear alkylbenzene synthesis directly from linear paraffins and benzene.

Table 2

Fixed-Bed Test Results with MCM-22 Type Catalysts[a]

Catalyst prepared in	Example 6	Example 7	Example 8	Example 9
Catalyst	0.6% Pt/MCM-22	0.6% Pt/MCM-22	0.6% Pt/MCM-49	0.6% Pt/MCM-56
Temp., °C	250	220	220	220
n-C_{16} LHSV, h^{-1}	0.15	0.10	0.10	0.10
Days on stream	9.0	27.8	15.8	24.6
n-C_{16} Conv, %	7.4	27.6	28.2	25.4
Benz. Conv, %	2.3	8.5	7.9	8.9
n-C_{16} utilization, %				
Light paraffins & light alkylbenzenes	14.5	19.2	23.4	14.7
Iso-C_{16}	9.1	8.7	11.6	13.0
C_{16}-Bz	76.1	65.2	57.4	63.2
Others[b]	0.3	6.9	7.6	9.1
Benzene utilization, %				
c-C_6 and c-C_{12}[c]	19.5	40.3	45.4	55.3
Light alkylbenzenes	22.3	16.5	18.4	9.4
C_{16}-Bz	56.9	38.6	31.1	30.2
Others[b]	1.3	4.5	5.1	5.1
Hexadecylbenzene ratio, % (L-C_{16}-Bz: linear hexadecylbenzene)				
2-Bz-C_{16}/all C_{16}-Bz	15	39	40	43
L-C_{16}-Bz/all C_{16}-Bz	66	97	96	96

a. 750 psig, 6:1 benzene/n-hexadecane molar ratio. Bz is benzene.

b. C_{12}-tetralins, C_{13}-indanes, C_{12}-naphthalenes, and traces of diphenyl hexadecanes were detected.

c. From benzene hydrogenation and hydrodimerization with hydrogen generated during n-hexadecane/benzene alkylation.

Data for Pt/ZSM-12 are shown in Table 3 below. Both alumina-bound and binder-free Pt/ZSM-12 were active for alkylation and isomerization.

Table 3

Fixed-Bed Test Results with ZSM-12

Catalyst prepared in	Example 10	Example 11
Catalyst	0.6% Pt/ZSM-12	0.6% Pt/ZSM-12
Binder	none	35% Al_2O_3
Temp., °C	300	230
n-C_{16} LHSV, h^{-1}	0.10	0.10
Days on stream	7.0	5.7
n-C_{16} Conv, %	30.9	68.1
Benz. Conv, %	1.5	5.8
n-C_{16} utilization, %		
Light paraffins & Light alkylbenzenes	13.2	15.3
Iso-C_{16}	81.0	64.8
C_{16}-Bz	5.8	19.2
Others[b]	0.0	0.7
Benzene utilization, %		
c-C_6 and C-C_{12}[c]	33.5	41.4
Light alkylbenzenes	40.0	21.1
C_{16}-Bz	16.7	28.3
Others[b]	9.7	9.2
Hexadecylbenzene ratio, % (L-C_{16}-Bz: linear hexadecylbenzene)		
2-Ph-C_{16}/all C_{16}-Bz	48	33
L-C_{16}-Bz/all C_{16}-Bz	77	50

a. 750 psig, 6:1 benzene/n-hexadecane molar ratio. Bz is benzene.

b. C_{12}-tetralins, C_{13}-indanes, C_{12}-naphthalenes, and traces of diphenyl hexadecanes were detected.

c. From benzene hydrogenation and hydrodimerization with hydrogen generated during n-hexadecane/benzene alkylation.

Table 4 below shows the data for Pt/ZSM-5, Pt/ZSM-23, and Pt/mordenite. Again,all the catalysts were very active for alkylation and isomerization.

Table 4

Fixed-Bed Test Results[a]

Catalyst prepared in	Example 12	Example 13	Example 14
Catalyst	0.4% Pt/ZSM-5	0.6% Pt/ZSM-23	0.6% Pt/Mordenite
Temp., °C	250	250	220
n-C_{16} LHSV, h^{-1}	0.1	0.1	0.1
Days on stream	2.7	1.9	8.8
n-C_{16} Conv, %	24.9	45.7	49.5
Benz. Conv, %	4.2	6.0	12.2
n-C_{16} utilization, %			
Light paraffins & light alkylbenzenes	82.3	79.9	67.9
Iso-C_{16}	16.6	19.8	17.4
C_{16}-Bz	1.1	0.4	14.1
Others[b]	0.0	0.0	0.6
Benzene utilization, %			
c-C_6 and c-C_{12}[c]	2.6	2.2	11.6
Light alkylbenzenes	74.3	89.2	70.8
C_{16}-Bz	0.9	0.2	9.4
Others[b]	22.1	8.5	8.1
Hexadecylbenzene ratio, % (L-C_{16}-Bz: linear hexadecylbenzene)			
2-Bz-C_{16}/all C_{16}-Bz	100	100	37
L-C_{16}-Bz/all C_{16}-Bz	100	100	84

a. 750 psig, 6:1 benzene/n-hexadecane molar ratio. Bz is benzene.

b. C_{12}-tetralins, C_{13}-indanes, C_{12}-naphthalenes, and traces of diphenyl hexadecanes were detected.

c. From benzene hydrogenation and hydrodimerization with hydrogen generated during n-hexadecane/benzene alkylation.

EXAMPLE 20

Batch Catalyst Screening for n-Hexadecane and Benzene Reaction

Molecular sieve catalysts as prepared in Examples 15, 16, and 17 were tested for n-hexadecane/benzene reaction in batch experiments. The catalysts data are shown in Table 5 below. The following general procedures were used for the batch experiments.

1.5 g of catalyst, ground to powder, was weighed in to a 300 cc autoclave. The autoclave was sealed and the catalyst was pretreated with 100 cc/min of flowing hydrogen for 2 hours at 350°C and 1 atm without stirring. The autoclave was cooled to room temperature and hydrogen was turned off. 58 g of benzene and 30 g of n-hexadacane were added to the autoclave *via* a s. s. vessel with nitrogen head pressure. The system was purged with 100 cc/min of flowing nitrogen for 10 min at 1 atm. The mixture was heated up to 250°C with stirring and kept at 250°C. Samples were taken at ~4 hr internals for off-line GC analysis. Representative data are shown in Table 5 below.

Again, the results show that these catalysts were active for aromatic alkylation with paraffins and paraffin isomerization.

Table 5

Batch Test Results of n-Hexadecane/Benzene Reaction[a]

Catalyst prepared in	Example 15	Example 16	Example 17
Catalyst	0.5% Pt M41S	0.6% Pt Zeolite Beta	1.0% Pt Sn/ZSM-5
Hours on stream	48	48	41
n-C_{16} Conv, %	10.0	41.7	1.5
Benz. Conv, %	4.7	11.0	0.2
n-C_{16} utilization, %			
Light paraffins & light alkylbenzenes	6.2	31.5	17.3
Iso-C_{16}	23.8	25.5	79.2
C_{16}-Bz	68.6	40.8	3.5
Others[b]	1.4	2.2	0.0
Benzene utilization, %			
c-C_6 and c-C_{12}[c]	2.2	11.6	-
Light alkylbenzenes	14.2	45.3	-
C_{16}-Bz	81.9	40.8	-
Others[b]	1.7	2.2	-
Hexadecylbenzene ratio, % (L-C_{16}-Bz: linear hexadecylbenzene)			
2-Bz-C_{16}/all C_{16}-Bz	15.1	9.1	31.3
L-C_{16}-Bz/all C_{16}-Bz	65.5	45.8	100.0

a. 250 C, autogenous pressure, 5.6 benzene/n-C_{16} molar ratio, 5 wt.% cat./n-C_{16}, no H_2. Bz is benzene.

b. C_{12}-tetralins, C_{13}-indanes, C_{12}-naphthalenes, and traces of diphenyl hexadecanes were detected.

c. From benzene hydrogenation and hydrodimerization with hydrogen generated during n-hexadecane/benzene alkylation.

EXAMPLE 21

Batch 1-Hexadecene and Benzene Reaction with Pt-Free MCM-22

A mixture of 58 g of benzene (99% purity), 30 g of 1-hexadecene (92% purity), 1.5 g of binder-free MCM-22 powder was stirred in a glass flask at 80°C for 21 hours. The catalyst was filtered off. Benzene was removed by a rotavap or and unreacted 1-hexadecene was removed by a Kugelrohr. A 34.8 g (93.5% yield) of hexadecylbenzene was recovered. GC analysis showed that the product contained 100% linear hexadecylbenzene with 48% 2-Ph-C_{16}, 30% 3-Ph-C_{16}, 5% 4-Ph-C_{16}, and the rest being 5- to 8-Ph-C_{16} isomers in roughly equal amount. Linear hexadecylbenzene properties are shown in Table 6 below.

EXAMPLE 22

Comparison of Product Properties

Table 6 below compares properties of hexadecylbenzene concentrates generated from hexadecane/benzene reaction over Pt/USY and Pt/MCM-22 with those of severely hydrocracked base stocks (U.S. Patent No. 4,419,220) and those generated from regular 1-hexadecene/benzene reaction over Pt-free MCM-22. The hexadecylbenzene concentrates were obtained by removing excess benzene from the total product mixture with a rotavapor, followed by a Kugelrohr separation under vacuum to remove unreacted n-hexadecane or 1-hexadecene. A small fraction of linear hexadecylbenzene was evaporated with unreacted n-hexadecane or 1-hexadecene during the Kugelrohr separation.

Table 6

Comparison of Product Properties: C_{16}-Bz *vs.* MWI Product

Catalyst		Pt-free MCM-22	Pt/USY	Pt/MCM-22
Reactants		1-$C_{16}^{=}$/benzene	n-C_{16}/benzene	n-C_{16}/benzene
Product	Severely Hydrocracked Base Stocks	C_{16}-Bz Concentrate	C_{16}-Bz Concentrate	C_{16}-Bz Concentrate
Product Contents				
	Paraffins & Cyclics	100% linear C_{16}-Bz	7% n-C_{16} 61% linear C_{16}-Bz 24% branched C_{16}-Bz 8% others	0.3% n-C_{16} 81% linear C_{16}-Bz 8% branched C_{16}-Bz ~11% others
Product Property				
kV @ 100°C, cSt	5 and 8	2.4	2.5	2.5
VI	140^{+}	121	80	96
Pour Point, °C	-12 to -18	-21	-36	-35

The hexadecylbenzene products produced with Pt/USY or Pt/MCM-22 has lower pour points (-35 to -36°C) than the severely hydrocracked base stocks (XHQ) or simple linear hexadecylbenzene. (-12 to -18°C or -21°C).

CLAIMS:

1. A process for direct alkylation of an aromatic hydrocarbon with an alkane comprising contacting a feed comprising an aromatic hydrocarbon and an alkane having at least 15 carbon atoms with a catalyst comprising a molecular sieve material having an incorporated metal component.

2. The process of claim 1 wherein the direct alkylation of aromatic hydrocarbons with alkanes is in the absence of the addition of olefins or functionalized alkanes.

3. The process of claim 1 wherein the molecular sieve material is selected from mordenite, ZSM-5, ZSM-12, ZSM-23, ZSM-48, Zeolite Beta, USY, MCM-22, MCM-36, MCM-49, MCM-56, M41S, and MCM-41.

4. The process of claim 1 wherein the metal component is selected from metals of Groups VIA, VIIA and VIIIA of the Periodic Table of Elements (IUPAC).

5. The process of claim 4 wherein the metal component comprises platinum or palladium or mixtures thereof.

6. The process of claim 4 wherein the platinum or palladium metal comprises from 0.01 to 10 wt.% of the catalyst.

7. The process of claim 1 wherein said contacting step is effected under conditions comprising a temperature from 100°C to 400°C, a pressure from atmospheric to 2500 psig, a space velocity from 0.01 to 100 LHSV, and a molar feed ratio of aromatics/alkanes from 0.1 to 30.

8. The process of claim 7 wherein the feed molar ratio of aromatics/alkanes is from 1.5 to 10.

9. The process of claim 1 wherein the process further comprises alkane isomerization.

10. The process of claim 1 wherein the alkanes comprise 15 to 22 carbon atoms.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/10828

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07C 2/64, 5/13
US CL :585/446, 467, 750, 751
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/446, 467, 750, 751

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,899,008 A (LAPIERRE et al) 06 February 1990, Abstract.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O"	document referring to an oral disclosure, use, exhibition or other means		
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