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# MANGANESE REFORMING OXIDE-CONTAINING CATALYST

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This invention relates to a process for the conversion of hydrocarbons to more desirable hydrocarbons in contact with a novel and improved catalyst comprising platinum and/or palladium deposited on a manganese oxide-promoted cracking component as a support.

Numerous processes have been proposed for the conversion or reforming of hydrocarbon fractions boiling within the motor fuel or naphtha range to increase the aromaticity and improve the anti-knock characteristics of said hydrocarbon fractions. These processes generally involve a number of simultaneously occurring reactions, such as isomerization, dehydrogenation, aromatization, and selective cracking. Such processes comprise the steps of passing a hydrocarbon fraction with or without added hydrogen over a reforming catalyst at elevated temperatures. The catalysts involved include a majority of the elements of the periodic table in various combinations, including platinum or palladium supported on a cracking catalyst, such as silica-alumina, or the like. While a number of these catalysts have been found to be effective, many have not been commercially adopted because they do not possess some of the desirable and necessary qualities of commercially feasible catalysts such as long life, immunity to poisoning, and ease of regeneration. The catalyst of the invention, hereinafter described, is effective in catalyzing the aforesaid reactions to effect improved yields.

The xylenes, namely orthoxylene, metaxylene, and paraxylene are important chemicals and find wide and varied application in industry. In some of these applications one of these specific isomers of xylene is very often superior to the other isomers or to mixtures of isomers. Unfortunately, the isomers of xylene and ethylbenzene are nearly always obtained as mixtures and the separation of the individual isomers from such mixtures is difficult and costly. Paraxylene is very often more desirable than the other xylene isomers and isomerization processes have been devised to isomerize ortho- and metaxylene and ethylbenzene to paraxylene. It is well known that xylenes can be isomerized by the use of such catalysts as aluminum chloride, boron fluoride, liquid hydrogen fluoride, and the like; however, processes employing these catalysts involve long contact times, cause a substantial amount of disproportionation of the feed, and result in low yields.

The principal object of the invention is to provide an improved process for catalytically converting hydrocarbon material to more desirable hydrocarbons. Another object of the invention is to provide an improved process for reforming hydrocarbon fractions falling within the motor fuel boiling range to form motor fuels of higher anti-knock rating in high yield. It is also an object to provide an improved process for isomerizing alkyl aromatic hydrocarbons in improved yield. A further object is to provide an improved process for isomerizing xylenes and/or ethylbenzene. Another object of the invention is to provide an improved process for isomerizing a mixture of ortho-, meta-, and paraxylenes of less than equilibrium concentration of paraxylene to produce a higher concentration of paraxylene in the mixture. Other objects of the invention will become apparent from a consideration of the accompanying disclosure.



In accordance with the invention, a catalyst composition comprising 0.1–5 weight percent platinum or palladium, 1–20 weight percent manganese oxide, and the remainder a cracking component is used for the conversion of hydrocarbon material to more desirable products and, particularly, for reforming petroleum distillates and isomerizing xylene fractions at a temperature in the range of 700–1000° F., pressure in the range of atmospheric to 1000 p. s. i. g., liquid hourly space velocity in the range of 0.3 to 10, and a hydrogen-hydrocarbon mol ratio of 0.5:1 to 20:1.

The present invention provides a catalyst and a reforming process employing said catalyst whereby a mixture of hydrocarbons containing substantial proportions of straight chain or branched chain paraffinic hydrocarbons and naphthenic hydrocarbons is converted into a mixture of hydrocarbons having an increased aromatic content in an improved yield. In the reforming process of this invention improved isomerization of alkyl cyclopentanes to cyclohexanes and dehydrogenation of these cyclohexanes to aromatics occurs without indiscriminate or uncontrolled cracking.

The catalyst of this invention is also very suitable for promoting the isomerization of alkyl aromatic hydrocarbons, such as the xylenes, without substantial disintegration and degradation of the hydrocarbons. Thus, a relatively pure xylene or a mixture of xylenes, which may contain ethylbezene, are isomerized to form particularly desirable isomers. A very useful conversion involves the isomerization of ortho- and meta-xylene in a mixture of xylenes to paraxylene in high yield. The catalyst of this invention is also effective in converting ethylbenzene, alone, or which may be present in the xylene mixture, to xylene in high yield.

The catalyst of the invention comprises, in general, a major proportion of cracking component, a minor proportion of manganese oxide, and a minor proportion of platinum or palladium. More specifically, the catalyst comprises a cracking component, 1–20 weight percent manganese oxide, and 0.1–5 weight percent platinum and/or palladium. More desirably, the catalyst comprises 5–15 weight percent manganese oxide and 0.2–1 weight percent platinum or palladium in addition to the cracking component. The cracking component, which acts as a support, carrier or extender for the catalytic agent, may be any cracking catalyst, either naturally occurring or synthetically produced. Naturally occurring materials include various aluminum silicates, particularly those which have been acid treated (Super Filtrol). Synthetically produced materials include silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, and the like. Fluorinated alumina, such as HF-treated alumina, is also a good support. The preferred cracking component in the catalyst of this invention is a synthetically produced silica-alumina.

Our catalyst may be prepared by methods known in the art, such as by impregnation or coprecipitation. The usual method of preparing this catalyst comprises impregnating the supporting material in the form of powder, granules, or pellets, with an aqueous solution of a suitable salt of manganese; drying and calcining the impregnated support by heating at an elevated temperature; impregnating the calcined manganese-impregnated support with an aqueous solution of a decomposable platinum or palladium compound; drying the impregnated composite; and reducing the platinum or palladium compound on the manganese oxide-impregnated support at an elevated temperature in a reducing atmosphere. The temperatures and the duration of the heating or calcining steps used are

not critical and are readily determined by one skilled in the art. Various procedures are known in the art for the preparation of the supporting material, which is commonly employed as a cracking catalyst in hydrocarbon conversion processes, and this supporting material may be prepared by any of these methods. A preferred method of forming the supporting material involves the coprecipitation of the hydrous oxides from a solution containing appropriate amounts of suitable soluble salts, separating the precipitated metal compounds, drying, calcining at an elevated temperature, and comminuting and forming the supporting materials into suitable shapes for contacting operations.

Reforming reactions utilizing the cracking component-supported platinum- or palladium-manganese oxide promoted catalyst of this invention may be performed with a wide variety of petroleum distillates, including naphtha, gasoline and the like. A naphtha boiling generally in the range of 150–350° F. is a very suitable feed stream. The reforming process is usually carried out at temperatures in the range of 700–1000° F. and preferably 800–950° F. The process is conducted at pressures in the range of atmospheric to 1000 p. s. i. g. and preferably 100–600 p. s. i. g. Liquid hourly space velocity may be in the range of 0.3–10 volumes of hydrocarbon per volume of catalyst per hour and a value in the range of 0.5–6 is preferred. The reaction is preferably carried out in the presence of hydrogen using a hydrogen-hydrocarbon mol ratio of 0.5:1 to 20:1 and preferably 1:1 to 10:1. The process of this invention may be effected in any suitable equipment and an especially suitable process is the fixed bed process in which the catalyst is used in the form of pellets or granules in a reaction zone and the hydrocarbon and hydrogen is passed through such zone in contact with the catalyst. After reforming, the products are fractionated to separate excess hydrogen, which is recycled to the reaction zone, and to recover the desired fractions of products.

Isomerization reactions employing the platinum- and/or palladium-manganese oxide-supported catalyst of this invention may very suitably be carried out with a xylene fraction using process conditions similar to those for reforming naphtha. The xylene fraction isomerized may be a substantially pure xylene; however, a xylene fraction containing ortho-, meta- and paraxylene not in equilibrium concentration and ethylbenzene is suitable, since high conversions of ortho- and metaxylene to paraxylene and of ethylbenzene to xylene are realized with the catalyst of this invention.

The following examples are presented as illustrative of the invention and are not to be construed as imposing unnecessary limitations thereon.

## EXAMPLE 1

A catalyst containing 0.3 weight percent platinum, 9.1 weight percent manganese oxide, and 90.6 weight percent commercial 90 silica-10 alumina was tested for the isomerization of a xylene concentrate and compared to a catalyst containing 0.3 weight percent platinum and 99.7 weight percent 90 silica-10 alumina. Our catalyst was prepared by immersing 143 grams of the silica-alumina pills in 150 ml. of manganous nitrate solution made by diluting 75 ml. of 50 percent manganous nitrate solution with 75 ml. of water, draining off the excess solution, drying the impregnated pills at about 290° F. for 40 minutes, calcining the dried pills at 820° F. overnight, immersing 67.7 grams of the calcined pills in 100 ml. of chloroplatinic acid containing 7.11 grams of chloroplatinic acid in 500 ml. of water, draining off the excess solution, drying the pills at 290° F. overnight, and heating the pills at 850° F. in a stream of hydrogen overnight. The platinum-silica-alumina catalyst was prepared by impregnated commercial silica-alumina pills (same as used in our catalyst) with an aqueous solution of chloroplatinic acid, draining off the excess solution, drying the impregnated material at 210° F., and heating the dried material at 850° F. in a stream of hydrogen overnight.

The xylene concentrate used in determining the isomerization activity of these catalysts contained 2.9 volume percent toluene, 6.7 volume percent paraxylene, 42.4 volume percent metaxylene, 22.9 volume percent orthoxylene, 24.4 volume percent ethylbenzene and 0.7 volume percent heavier than xylenes. The data for these isomerization runs are presented in Table I and show the superior efficiency of the manganese oxide promoted catalyst.

*Table I.—Isomerization of xylenes fraction*

| | Pt-$MnO_2$-Silica-Alumina | Pt-Silica-Alumina |
|---|---|---|
| Run No. | 1 | 2 |
| Temperature, ° F. | 905 | 902 |
| Pressure, p. s. i. a. | 365 | 365 |
| LHSV | 3.1 | 3.2 |
| $H_2$/HC, mol | 3.9 | 4.1 |
| Products, wt. percent: | | |
| $C_5$ and lighter | 1.2 | 8.7 |
| Naphthenes | 3.1 | 2.6 |
| Benzene | 0.7 | 2.3 |
| Toluene | 5.5 | 12.8 |
| p-Xylene | 14.4 | 12.3 |
| m-Xylene | 34.9 | 26.8 |
| o-Xylene | 17.9 | 11.7 |
| Ethylbenzene | 19.5 | 11.3 |
| Heavier than xylenes | 2.8 | 11.5 |
| Total | 100.0 | 100.0 |

## EXAMPLE 2

A catalyst containing 0.3 weight percent platinum, 13.2 weight percent manganese oxide, and the remainder silica-alumina was tested for the reforming of a naphtha feed and compared to a platinum-silica-alumina catalyst containing 0.3 weight percent platinum. The naphtha feed contained 9 liquid volume percent aromatics and had a boiling range of 150–270° F. The reforming data obtained are given in Table II, and show that there was a substantially greater conversion of the naphtha to aromatics and a smaller conversion of the naphtha to gaseous products in the reforming run using the manganese oxide-containing catalyst.

*Table II.—Reforming naphtha*

| | Pt-Silica-Alumina | Pt-MnO-Silica-Alumina |
|---|---|---|
| Run No. | 3 | 4 |
| Temperature, ° F. | 885 | 893 |
| Pressure p. s. i. a. | 415 | 415 |
| LHSV | 3.6 | 3.5 |
| $H_2$/HC mol | 6.5 | 6.5 |
| Products, wt. percent: | | |
| $H_2$ | 1.5 | 0.8 |
| $CH_4$ | 0.2 | 0.5 |
| $C_2$'s | 0.5 | 0.6 |
| $C_3$'s | 8.1 | 4.5 |
| $C_4$'s | 15.5 | 9.8 |
| $C_5^+$ | 74.2 | 83.3 |
| Total | 100.0 | 100.0 |
| Aromatic, content of $C_5^+$, LV percent | 51.6 | 51.0 |

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

We claim:

1. A process for the catalytic conversion of a fluid hydrocarbon material to more valuable hydrocarbons which comprises contacting said material with a catalyst comprising a member of the group consisting of platinum and palladium in an amount in the range of 0.1 to 5 wt. percent, manganese oxide in the range of 1 to 20 wt. percent, and the balance a cracking component, under con-

version conditions which convert said hydrocarbon material into more valuable hydrocarbons.

2. The process of claim 1 wherein the cracking component is selected from the group consisting of acid activated aluminum silicate clay, silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, and fluorinated alumina.

3. The process of claim 2 wherein the hydrocarbon material comprises a petroleum distillate and reforming conditions including a temperature in the range of 700 to 1000° F., a pressure in the range of atmospheric to 1000 p. s. i. g., free hydrogen in admixture with the hydrocarbon, and a liquid hourly space velocity in the range of 0.3 to 10 volumes of hydrocarbon per volume of catalyst per hour, are maintained.

4. The process of claim 3 wherein the hydrocarbon material comprises a naphtha fraction boiling in the range of 150 to 350° F. and reforming conditions are maintained.

5. The process of claim 3 wherein hydrogen is fed to the reaction zone to maintain therein a hydrogen to hydrocarbon mol ratio in the range of 0.5:1 to 20:1.

6. The process of claim 2 wherein the hydrocarbon material comprises a xylene fraction of other than an equilibrium concentration and xylene isomerizing conditions are maintained.

7. The process of claim 1 wherein said hydrocarbon material comprises at least one isomerizable component; said conversion conditions are isomerizing and include a temperature in the range of 700 to 1000° F., a pressure in the range of atmospheric to 1000 p. s. i. g., and a liquid hourly space velocity in the range of 0.3 to 10 volumes of hydrocarbon per volume of catalyst per hour; and said cracking component is selected from the group consisting of acid-activated aluminum silicate clay, silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, and fluorinated alumina.



8. The process of claim 7 wherein said material comprises at least one xylene.

9. The process of claim 7 wherein said material comprises a mixture of xylenes in which ortho- and meta-xylenes are in a concentration in excess of equilibrium and a substantial proportion thereof is isomerized to paraxylene.

10. The process of claim 7 wherein said material comprises ethylbenzene and a substantial proportion of same is converted to xylenes.

11. A process for reforming a petroleum distillate which comprises contacting same in admixture with free $H_2$ under reforming conditions with a catalyst comprising platinum deposited on a silica-alumina support promoted with manganese oxide in the range of 1 to 20 weight percent of the catalyst, the platinum being in the range of 0.1 to 5 weight percent of the catalyst.

12. A process for isomerizing an isomerizable fluid hydrocarbon which comprises contacting same under isomerizing conditions with a catalyst comprising platinum deposited on a silica-alumina support promoted with manganese oxide in the range of 1 to 20 weight percent of the catalyst, the platinum being in the range of 0.1 to 5 weight percent of the catalyst.

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