May 4, 1971 R. L. JACOBSON 3,577,474

CONVERSION OF C_6-C_7 CYCLOALKANES TO BENZENE AND TOLUENE

Filed Nov. 18, 1968

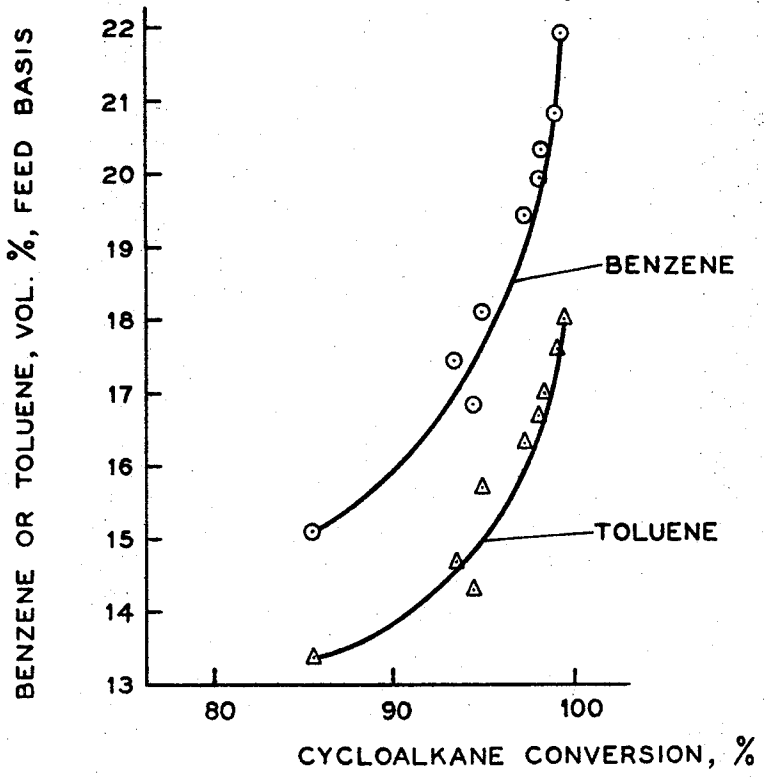


FIG. 1

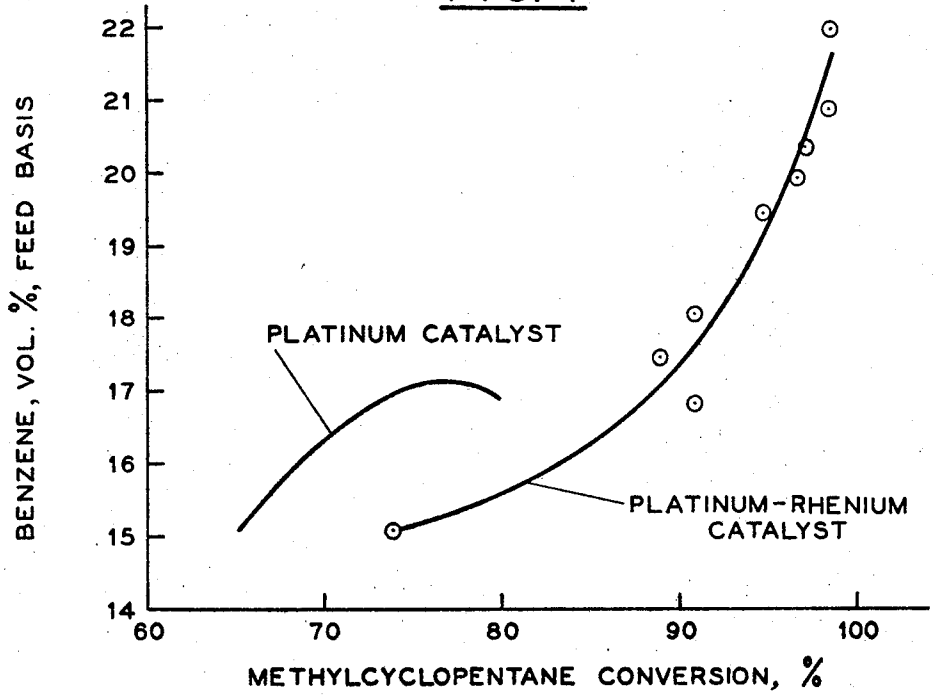


FIG. 2

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United States Patent Office 3,577,474 Patented May 4, 1971

3,577,474

CONVERSION OF C_6—C_7 CYCLOALKANES TO BENZENE AND TOLUENE

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Filed Nov. 18, 1968, Ser. No. 776,533
Int. Cl. C07c 15/04
U.S. Cl. 260—668 7 Claims

ABSTRACT OF THE DISCLOSURE

High conversion of C_6–C_7 cycloalkanes to aromatics is obtained by contacting the cycloalkanes in the presence of hydrogen with a catalyst comprising 0.01 to 3 weight percent platinum and 0.01 to 5 weight percent rhenium in association with a porous inorganic oxide carrier and maintaining the conversion conditions sufficiently severe to convert at least 85 percent, and preferably 90 percent, of the cycloalkanes to aromatics and alkanes.

BACKGROUND OF THE INVENTION

Field

This invention relates to the selective production of benzene and toluene from C_6–C_7 cycloalkanes. More particularly, the invention is directed to catalytic conversion of C_6–C_7 cycloalkanes to aromatics using a catalyst comprising platinum and rhenium supported on a porous inorganic oxide carrier.

Prior art

The demand for benzene and toluene is sufficiently great so that it is economically feasible to catalytically convert selected petroleum fractions to benzene and toluene. A typical process is the conversion of a C_6–C_7 fraction containing C_6–C_7 cycloalkanes to benzene and toluene using a platinum-alumina containing catalyst. The C_6–C_7 cycloalkane hydrocarbons are primarily cyclohexane, methylcyclopentane, dimethylcyclopentane, and methylcyclohexane. The reactions involved in the production of benzene and toluene include dehydrogenation of the cyclohexane and the methylcyclohexane to benzene and toluene, respectively; isomerization of methylcyclopentane to cyclohexane, followed by dehydrogenation to benzene; and isomerization of dimethylcyclopentane to methylcyclohexane, followed by dehydrogenation to toluene. The latter reactions are the more difficult; thus the conversion of methylcyclopentane and dimethylcyclopentane to benzene and toluene is characteristically relatively low. Hence, the yield of benzene and toluene in conventional commercial practice is generally lower than otherwise would be obtained if all the methylcyclopentane and dimethylcyclopentane were converted.

Competing with the C_6–C_7 cycloalkane conversion to benzene and toluene is the C_6–C_7 cycloalkane conversion to alkanes, e.g., heptane, hexane, pentane, butane, etc. More severe operations, that is, higher conversion of the cycloalkanes, particularly methylcyclopentane, does not necessarily result in higher yields of benzene and toluene, but may result in more alkanes being produced.

SUMMARY OF THE INVENTION

It has now been found that converting C_6–C_7 cycloalkanes in the presence of a catalyst comprising platinum and rhenium at severe conditions can be used to obtain high yields of benzene and toluene. Thus, it has been found that operating at high conversion levels of cycloalkanes to benzene and toluene plus alkanes, i.e., at conversion levels of at least 85 percent and preferably 90 percent, results in high yields of benzene and toluene.

Thus, in accordance with the present invention, C_6–C_7 cycloalkanes are converted to high yields of aromatics by contacting said cycloalkanes in the presence of hydrogen in a reaction zone with a catalyst comprising 0.01 to 3 weight percent platinum and 0.01 to 5 weight percent rhenium in association with a porous inorganic oxide carrier and at reaction conditions, including a pressure of from 50 to 750 p.s.i.g. and a temperature of from 700 to 1050° F., sufficiently severe to convert at least 85 percent of said cycloalkanes to aromatics and alkanes. Preferably less than 30 p.p.m. H_2O is present in said reaction zone and preferably less than 10 p.p.m. sulfur is present in said reaction zone.

BRIEF DESCRIPTION OF THE DRAWING

The present invention may be better understood and will be further explained hereinafter with reference to the graphs in FIGS. 1 and 2.

FIG. 1 shows the volume percent benzene and toluene produced as a function of the cycloalkane conversion to aromatics and alkanes using a platinum-rhenium catalyst. It is noted that the yields of benzene and toluene rapidly increase as the total cycloalkane conversion increases above 85 percent.

FIG. 2 shows for comparison purposes the benzene produced as a function of the methylcyclopentane conversion to benzene and alkanes for a process using a platinum catalyst without rhenium and a process using a platinum-rhenium catalyst. The benzene produced reaches a maximum at around 77 percent methylcyclopentane conversion for the process using the platinum catalyst. Thereafter, more severe conditions only result in alkanes being produced at the expense of benzene. On the other hand, the process using the platinum-rhenium catalyst results in greater quantities of benzene being produced as the severity of the operation is increased, i.e., as the conversion of methylcyclopentane to aromatics and alkanes is increased.

DESCRIPTION OF THE INVENTION

The catalyst which finds use in the cycloalkane conversion process of the present invention comprises a porous inorganic oxide carrier or support containing from 0.01 to 3 weight percent platinum and from 0.01 to 5 weight percent rhenium. Preferably from 0.1 to 3 weight percent halide is also present. Porous inorganic oxide carriers or supports useful in the present invention include a large number of materials with which the catalytically active amounts of platinum and rhenium can be disposed. Thus, the support can be natural or synthetically-produced inorganic oxides or combination of inorganic oxides. Typical acidic inorganic oxides which can be used are the naturally occurring aluminum silicates, particularly when acid treated to increase the activity, and the synthetically-produced cracking supports, such as silica-alumina, silica-zirconia, silica-alumina-zirconia, silica-magnesia, silica-alumina-magnesia, and crystalline zeolitic aluminosilicates. Generally, however, inorganic oxides such as magnesia and alumina are preferred. These supports have limited acidity. The inorganic oxide supports for purposes of the present invention must be porous, i.e., have a surface area of greater than 50 $m.^2/gm.$, preferably 50 to 700 $m.^2/gm.$, and more preferably from 150 to 700 $m.^2/gm.$

Alumina is particularly preferred for purposes of this invention. The alumina can be prepared by a variety of methods satisfactory for purposes of this invention. Preparation procedures for alumina are well known in the art.

Various methods of preparation can be used for associating the platinum and rhenium with the porous inorganic oxide carrier. Platinum and rhenium can be disposed on the porous inorganic oxide in intimate admixture with each other by such suitable techniques such as ion-exchange, coprecipitation, impregnation, etc. It is not neces-

sary that both metals be incorporated onto the porous inorganic oxide by the same technique. Thus, one of the metals can be associated wtih the carrier by one method such as, for example, coprecipitation, and the other metal associated with the carrier by another technique such as, for example, impregnation. Furthermore, the metals can be associated with the carrier either simultaneously or sequentially. It is generally preferred that the metals be associated with the carrier by impregnation, either sequentially or simultaneously. In general, the carrier material is impregnated with an aqueous solution of a decomposable compound of the metal in sufficient concentration to provide the desired quantity of metal in the finished catalyst. To incorporate platinum on the catalyst by impregnation, chloroplatinic acid is preferred. Other platinum-containing compounds can be used, e.g., chloroplatinates and polyamineplatinum salts. Rhenium is suitably incorporated onto the carrier by impregnation with perrhenic acid. However, ammonium or potassium perrhenates, among others, can also be used.

It is contemplated in the present invention that incorporation of the metals with the carrier can be accomplished at any particular stage of the catalyst preparation. For example, if the metals are to be incorporated onto an alumina support, the incorporation can take place while the alumina is in the sol or gel form. Alternatively, a previously prepared alumina carrier can be impregnated with a water solution of the metal compounds. Generally, the catalyst is preferably prepared by impregnating the metals onto a previously prepared porous inorganic oxide carrier. The metals are desirably uniformly distributed on the surface of the carrier and are preferably in intimate admixture with each other on the carrier.

The platinum-rhenium catalyst should comprise platinum in an amount from 0.01 to 3 weight percent and more preferably, from 0.2 to 1 weight percent based on the finished catalyst. The concentration of rhenium in the finished catalyst composition is preferably in the range of from 0.01 to 5 weight percent and more preferably, from about 0.1 to 2 weight percent. It is preferred that the rhenium to platinum atom ratio be from 0.2 to 2 and more preferably, that the atom ratio of rhenium to platinum not exceed one.

After incorporating platinum and rhenium onto the porous inorganic oxide carrier, the resulting composite is usually dried by heating at a temperature of no greater than about 500° F. and preferably from about 200° F. to 400° F. If the metals are sequentially incorporated onto the porous inorganic oxide support, the catalyst may be dried after the addition of the first metal but before the addition of the other. Furthermore, the catalyst composite containing only one metal can be calcined at an elevated temperature, e.g., up to about 1200° F., if desired, prior to incorporation of the other metal component. Generally, however, calcination at an elevated temperature, e.g., from 700° F. to 1200° F., is done only after both metals have been incorporated onto the carrier and the composite dried.

Prior to use in the present process the catalyst comprising platinum and rhenium is heated in the presence of hydrogen to reduce the metals; preferably dry hydrogen is used although other reducing agents could be used. In particular, it is preferred that the prereduction be accomplished at a temperature in the range of 600° F. to 1300° F. and preferably from 600° F. to 1000° F.

The catalyst used in the present invention preferably has a limited amount of acidity. Thus, the catalyst preferably contains a halide and more preferably, a chloride or fluoride. Bromides can also be used. The halide should be present in an amount from 0.1 to 3 weight percent total halide content and preferably from 0.1 to 2 weight percent. The halide can be incorporated onto the catalyst carrier at any suitable stage of catalyst manufacture, e.g., prior to or following incorporation of the platinum and rhenium. Generally, halide is incorporated onto the carrier in the process of impregnating metals onto the carrier; e.g., impregnating the carrier with chloroplatinic acid normally results in chloride addition to the carrier. However, more halide may be desired, in which case additional halide can be incorporated onto the support simultaneously with the incorporation of the metal or following incorporation of the metal. In general, halides are combined with the catalyst carrier by contacting suitable compounds such as hydrogen fluoride, ammonium fluoride, hydrogen chloride or ammonium chloride, using the gaseous form or a water soluble form, with the carrier. Preferably, the halide is incorporated onto the carrier from an aqueous solution containing said halide.

The C_6–C_7 fraction which is used in the present process will preferably boil within the range of from 154° F. to 215° F. The C_6–C_7 fraction should contain at least about 20 volume percent C_6–C_7 cycloalkanes and preferably at least about 40 volume percent C_6–C_7 cycloalkanes. Preferably the fraction will contain at least 10 volume percent methylcyclopentane and more preferably 20 volume percent methylcyclopentane. Thus, while other components may be present in the C_6–C_7 fraction, for example, hexane and heptane, the present process involves the conversion of the C_6–C_7 cycloalkanes in the fraction to benzene and toluene. The selected fraction will generally be obtained by fractionating a hydrocracked feedstock.

It is preferred that the sulfur level in the reaction zone be less than about 10 p.p.m. and preferably less than about 2 p.p.m. The sulfur level in the reaction zone is determined as parts by weight of sulfur to parts by weight of feed and recycle gas or once-through hydrogen, as the case may be, at the inlet to the reaction zone. Thus, when a recycle hydrogen-rich gas stream is used in the process, the sulfur is defined with respect to the feed and recycle gas plus any make-up hydrogen. If a recycle gas stream is not used, then the sulfur level is defined with respect to feed and once-through hydrogen. Actual measurement of sulfur present in the reaction zone as above defined may be done by individually measuring by conventional means the sulfur in the feed and the sulfur in the recycle gas stream and totaling the values obtained. It is understood that sulfur initially adsorbed on the catalyst, for example, present as metal sulfides, is not considered in determining the sulfur level in the reaction zone.

In order to maintain the low levels of sulfur in the reaction zone, the feed to the reaction zone must preferably be relatively free of sulfur. Preferably the C_6–C_7 fraction should contain less than 10 p.p.m. sulfur to feed, by weight. Generally, if the feed contains high concentrations of sulfur, acceptable levels can be reached by hydrogenating the feedstock in a presaturation zone using a hydrogenation catalyst which is resistant to sulfur poisoning. Organic sulfur in the feed is converted to hydrogen sulfide which can then be removed by suitable conventional processes, such as using molecular sieve adsorbents, fractionation processes, etc. Suitable hydrodesulfurization conditions include a temperature of from 700–850° F., a pressure of from 200 to 2000 p.s.i.g., and a liquid hourly space velocity of from 1 to 5. Usually, a wide boiling range hydrocarbon fraction, e.g., a naphtha fraction boiling in the range from 75 to 550° F., is treated to remove sulfur, then fractionated to obtain a C_6–C_7 cut. It is understood, however, that the C_6–C_7 cut may be obtained first, followed by treatment to remove sulfur impurities.

When operating under the preferred embodiment of having low sulfur in the reaction zone, it is necessary to prevent sulfur from building up in the hydrogen recycle stream. The hydrogen recycle stream can be passed through an adsorption zone, for example, a molecular sieve, preferably a sieve having pore diameters of about 4 angstroms, prior to introduction into the reaction zone. Other adsorbents besides molecular sieves can be used to adsorb sulfur contaminants such as H_2S. Thus, for

example, zinc oxide and supported nickel- molybdenum oxides can be used as the adsorption media. When operating without a recycle hydrogen stream, once-through hydrogen to the reaction zone should preferably be relatively free of sulfur.

It is also preferred for purposes of the present invention that the water content in the reaction zone not exceed about 30 p.p.m. water to feed and recycle gas or once-through hydrogen, by weight. For a dry operation the feed should be substantially free of water, that is, contain less than 30 p.p.m. Water can be removed from the feed by passing the feed through an adsorption zone, for example, a molecular sieve, prior to contacting the catalyst in the reaction zone. Also, where a recycle hydrogen stream is used adsorption means can be used to prevent water from building up in the recycle gas stream. Generally, the adsorption means used to remove sulfur in the recycle stream can also be used to remove water. For example, a molecular sieve in the recycle hydrogen stream will substantially remove all of the water and sulfur admixed with the hydrogen.

The reaction conditions used in the conversion of cycloalkanes to benzene and toluene should include a pressure of from 50 to 750 p.s.i.g., preferably 50 to 500 p.s.i.g., and a temperature of from 700 to 1050° F., preferably 750 to 1000° F. The liquid hourly space velocity (LHSV), i.e., the volume of feed per volume of catalyst per hour (v./v./hr.), should range from 0.1 to 10, preferably 0.5 to 5. The conversion process should be conducted in the presence of hydrogen; preferably the hydrogen to feed mole ratio should be from 0.5 to 20. The reaction condtions should be sufficiently severe to convert at least 85 percent and preferably 90 percent of the C_6–C_7 cycloalkanes to aromatics, i.e., benzene and toluene, and alkanes. That is to say, based on the feed, 85 percent and preferably 90 percent of the C_6–C_7 cycloalkanes should be converted to other compounds during the conversion process. The high conversion of the C_6–C_7 cycloalkanes can be obtained by correlating the reaction conditions, for example, by increasing the temperature, lowering the pressure, lowering the space rate, etc.

Example

A composite comprising 0.6 weight percent platinum on alumina was impregnated with a solution of perrhenic acid of sufficient concentration to give the finished catalyst a rhenium concentration of 0.6 weight percent. The catalyst also contained 0.6 weight percent chloride. The platinum-rhenium catalyst was tested for C_6–C_7 cycloalkane conversion to benzene and toluene.

The C_6–C_7 fraction containing C_6–C_7 cycloalkanes had the following composition:

TABLE

Benzene	1.6
Toluene	1.0
Methylcyclopentane	21.9
Cyclohexane	8.8
Dimethylcyclopentane	13.4
Methylcyclohexane	5.0
C_6–C_7 alkanes	48.3

The feed was contacted with the catalyst at a pressure of 250 p.s.i.g., a liquid hourly space velocity of 2.5, and a hydrogen to hydrocarbon mole ratio of about 3. The temperature was varied to increase the severity of operation, that is, to increase the total conversion of C_6–C_7 cycloalkanes to aromatics and alkanes. Less than 30 p.p.m. H_2O and less than 10 p.p.m. sulfur were present in the reaction zone during the process.

The volume percent benzene and toluene in the product as a function of C_6–C_7 cycloalkane conversion was measured and is shown in FIG. 1. The benzene and toluene yields are shown on a feed basis which takes into account changes in density of the product. It is observed that the yields of benzene and toluene significantly increased as the total conversion of cycloalkanes increased above about 85 percent and preferably 90 percent. Thus, at very severe operations the present process is selective for the production of benzene and toluene.

The conversion of methylcyclopentane to benzene was also measured and the results shown in FIG. 2. The volume percent benzene in the product is shown as a function of methylcyclopentane conversion. The volume percent benzene includes not only the benzene resulting from the conversion of methylcyclopentane but also includes the benzene produced by the conversion of cyclohexane. For comparison purposes, the conversion of methylcyclopentane to benzene using a platinum catalyst comprising 0.38 weight percent platinum, 0.2 weight percent fluoride, and 0.5 weight percent chloride is also shown. Similar reaction conditions were used for process using the platinum catalyst as for process using the platinum-rhenium catalyst. The process using the platinum catalyst was conducted under conditions wherein 400 p.p.m. water and several p.p.m. H_2S were present in the recycle gas. While it is expected that the presence of water and sulfur would change the location of the maximum benzene produced, it is not believed that the removal of water or H_2S from the process using the platinum catalyst would significantly change the shape of the curve.

It is noted that the benzene production reaches a maximum for the process using the platinum catalyst at about 77 percent methylcyclopentane conversion; thereafter more severe operations result in significant increases in alkanes to the expense of benzene production. On the other hand, the benzene produced using the platinum-rhenium catalyst significantly increases as the methylcyclopentane conversion increases.

The foregoing disclosures of this invention are not to be considered as limiting since many variations can be made by those skilled in the art without departing from the scope or spirit of the appended claims.

I claim:

1. A process for catalytically converting a C_6–C_7 cycloalkane fraction that contains at least ten volume percent methylcyclopentane to selectively form aromatics comprising:

converting at least 85 percent of the C_6C_{-7} cycloalkanes to aromatics and alkanes at reaction conditions including contacting the C_6–C_7 cycloalkane fraction with hydrogen and a catalyst comprising 0.01 to 3 weight percent platinum and 0.01 to 5 weight percent rhenium in association with a porous solid carrier in a reaction zone at a pressure from 50 p.s.i.g. to 750 p.s.i.g. and a temperature from 700° F. to 1050 F.

2. The process of claim 1 wherein less than 30 p.p.m. H_2O is present in said reaction zone.

3. The process of claim 1 wherein less than 10 p.p.m. sulfur is present in said reaction zone.

4. The process of claim 1 wherein said catalyst contains 0.1 to 3 weight percent halide.

5. The process of claim 1 wherein said cycloalkanes comprise predominantly methylcyclopentane.

6. The process of claim 1 wherein at least 90 percent of said C_6–C_7 cycloalkanes are converted to aromatics and alkanes.

7. A process as in claim 1 wherein at least 90 percent of the C_6–C_7 cycloalkanes are converted to other compounds.

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U.S. Cl. X.R.

208—138