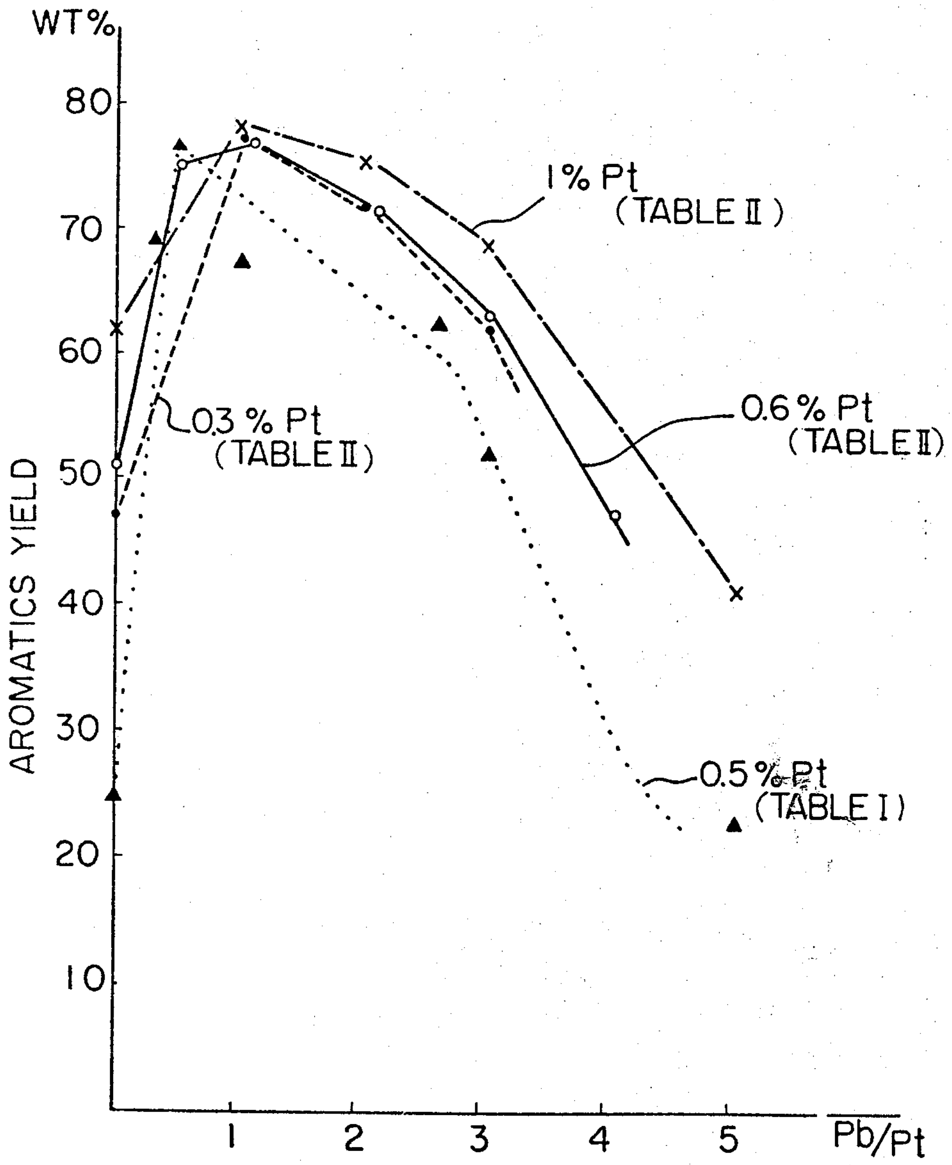
Aug. 6, 1974 NAOYA KOMINAMI ET AL 3,827,988

PT-Pb CATALYST COMPOSITIONS

Filed Nov. 18, 1971



United States Patent Office

3,827,988

Patented Aug. 6, 1974

3,827,988

Pt-Pb CATALYST COMPOSITIONS

Naoya Kominami, Tokyo, and Toshiyuki Iwaisako and Kusuo Ohki, Saitama, Japan, assignors to Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan

Continuation-in-part of application Ser. No. 6,948, Jan. 29, 1970. This application Nov. 18, 1971, Ser. No. 200,065

Claims priority, application Japan, Feb. 10, 1969, 44/9,488; Aug. 28, 1969, 44/67,617; Dec. 25 1969, 44/103,817

Int. Cl. B01j *11/78*

U.S. Cl. 252—441 15 Claims

ABSTRACT OF THE DISCLOSURE

Pt-Pb catalyst compositions containing specified amounts of Pt and Pb in specified ratios and prepared by particular impregnation procedures are effective hydroforming catalysts.

RELATED APPLICATIONS

This application is a continuation-in-part of our application Ser. No. 6,948, filed Jan. 29, 1970. It is related to applications: Ser. No. 200,064 which describes hydroforming of a hydrocarbon charge with the catalysts described in this application; Ser. No. 200,023 which describes hydroforming of a hydrocarbon charge with a Pt-Pb catalyst prepared by a sequential impregnation method wherein Pt is first supported on a carrier prior to supporting Pb on the carrier; and Ser. No. 200,071 which describes hydroforming of a hydrocarbon charge with a Pt-Pb catalyst prepared by coprecipitation; all filed concurrently herewith.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a Pt-Pb catalyst compositions which can also contain one or more other catalytic components, and to methods for their preparation. It is also concerned with a method of producing a distillate of high aromatic concentration in high yield by highly selectively subjecting naphthenic hydrocarbons ot dehydrogenation and paraffinic hydrocarbons to dehydrocyclization, by contacting such hydrocarbons with the catalysts.

Description of the Prior Art

A number of investigations have been made heretofore on methods for producing aromatic hydrocarbons from petroleum sources to establish several industrial processes employing catalysts comprising platinum, chromina, molybdena and the like. In these processes, naphtha is used as the starting material, which is subjected to catalytic reaction in gas phase at a high temperature. The liquid product thus produced contains isomers of paraffinic hydrocarbons at a high concentration and is often used as gasoline for motor cars, etc. because of its high octane number. However, its content of aromatic hydrocarbons is so low that an additional extraction or dealkylation step is needed in order to obtain benzene, toluene, xylenes and the like. In addition, the yield of aromatic hydrocarbons based on the starting material employed is so low that the operation of these steps is costly.

On the other hand, demand for aromatic hydrocarbons is being increased rapidly due to rapid growth of industries related to aromatics such as plastic and synthetic fiber industries. In this respect, it has become necessary to develop a process for producing aromatics in a higher yield. Moreover, the gasoline industry needs higher and higher octane numbers.

However, the existing processes will be associated with more expensive products if the yield of aromatics or the octane number is improved, and they are hardly feasible from the industrial point of view. Cracked gasoline, a by-product in the production of ethylene, which is one of the favorable sources for aromatics, is limited in the amount of production because it depends upon the production of ethylene.

SUMMARY OF THE INVENTION

As a result of extensive investigations on the process commercially advantageous in consideration of the source and demand of aromatics as well as the process economy as mentioned above, we have discovered a process with many advantages including the improved yield of aromatics. The present invention, derived from the discovery, is concerned with a method of producing aromatic hydrocarbons which comprises treating a hydrocarbon or a hydrocarbon mixture at a temperature from 300° C. to 650° C. over a catalyst comprising platinum and lead or a catalyst comprising platinum, lead and at least a member selected from lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, germanium, bismuth, chromium, molybdenum, tungsten, uranium, rhenium, ruthenium, rhodium, palladium, osmium and iridium. The catalyst is prepared by an impregnation procedure.

According to this invention, a variety of advantages may be enjoyed as compared with prior methods as set forth below.

First, benzene, toluene, xylenes and polymethylbenzenes are produced by quite simple procedures at low cost because of high concentration and yield of aromatics in the reformate produced according to this invention. For example, a distillate of higher boiling point than toluene or xylene in the reaction product contains neither paraffin nor naphthene and then separation can be effected by distillation only, without application of solvent extraction. Such a distinction from the prior processes is ascribed to high activity and selectivity of the catalyst of this invention in terms of aromatic formation, namely dehydrogenation or dehydrocyclization reactions.

In other words, in the conventional reforming processes known heretofore, since hydrocracking, isomerization, dehydrogenation or dehydrocyclization are the main reaction involved, an attempt to obtain a liquid fraction having a high aromatic concentration leads to an increase in hydrocracking with attendant results in low liquid yield and degraded economy. If on the other hand, the liquid yield is made higher, then the paraffin concentration in the resulting liquid becomes higher.

However, when the catalyst of the present invention is employed, quite unexpectedly, hydrocracking and isomerization are suppressed remarkably while dehydrogenation of naphthene or dehydrocyclization of paraffin preferentially occurs, and, in addition, the catalyst activity is quite high.

While lead has been shown to be a poison for a platinum catalyst in hydroforming catalysts (U.S. Pat. No. 3,000,811 of Murray et al.), it has been found that particular Pt-Pb combinations containing specified Pb contents in specified Pb/Pt ratios are excellent hydroforming catalysts. If the amount of Pb supported on a carrier with Pt is excessive, Pb exhibits a poisoning effect. Also, if the ratio of Pb to Pt on a carrier exceeds a specified value, then the Pt catalyst is poisoned. Influencing the effectiveness of the catalysts also is the method by which they are prepared. Surprisingly, then, when the amount of Pb is controlled within prescribed limits, the Pb/Pt ratio is also so controlled, and a particular method of preparation is selected, hydroforming catalysts of high activity and high selectivity can be obtained.

Thus, utilization of features of the present invention as described above serves to produce aromatics having high carbon numbers from high boiling fractions having high carbon numbers such as, for example, kerosene and gas oil, in high yields. The same thing applies to naphtha and the process of the present invention affords far higher yields in the production of trimethylbenzene, durene and the like than known processes.

Secondly, purity and yield of hydrogen are so high that hydrogen can be supplied at a low cost.

Thirdly, life of the catalyst of this invention is so long that frequency in regeneration of the catalyst is reduced under normal reaction conditions in industrial operation.

Fourthly, the catalyst of this invention is operative at lower pressures than in prior processes. As the rate of degradation in activity in the prior catalysts is much more drastic and they become inoperative during long operation, and, therefore, the process on an industrial scale has to be carried out under high pressures. On the contrary, the catalyst of this invention is stable in the course of a long operation to give a high yield of aromatics.

As the platinum component of the catalyst, there may be used, for example, the hydroxide, platinum halides, chloroplatinic acid or hydrate or ammonium salt thereof. Especially preferred are substances containing a halogen. This is due to the fact that in a compound containing platinum and halogen, the halogen and especially chlorine present in the compound advantageously contribute to the catalytic activity like in other platinum reforming catalysts. The preferable amount of chlorine contained in the catalyst of the present invention is in the range of 0.1–2.0% by weight and particularly in the range of 0.5–1.5% by weight based on the total weight of catalyst components. As the lead component, there may be employed halogenides, inorganic and organic salts, hydroxide, oxide and the like. The element used as the third component may be in the form of its oxide, hydroxide, halide or other inorganic and organic salt or complex. The platinum, lead and the third components may be in the form of a salt containing each of them.

Contents of the platinum, lead and the third components are 0.01–5% by weight, 0.01–5% by weight and 0–3% by weight, respectively, and preferably 0.05–1% by weight, 0.05–3% by weight and 0–1% by weight, respectively based on the total weight of catalyst components, with the ratio of lead to platinum ranging from 0.1 to 3.

The catalyst is prepared by simultaneously supporting platinum and lead on a carrier by conventional impregnation methods; or by supporting lead on a carrier and thereafter supporting platinum on the carrier, again using conventional impregnation methods. Preferred Pb/Pt ratios, lead and platinum contents, and third component content with the two impregnation methods, are as follows:

	Simultaneous impregnation	Pb, then Pt impregnation
Pb, percent wt	0.1–2	0.1–2.5
Pt, percent wt	0.1–1	0.1–1
Pb/Pt	0.3–2	0.3–2.5
3d component, percent wt	0–1	0–1

In the simultaneous impregnation method, a carrier is immersed in a solution (normally an aqueous solution) containing platinum and lead components, thereby supporting both of said components simultaneously on the carrier. The amount of solution used is preferably from 1 to 10 volumes per volume of the carrier for economical reasons. After the catalyst components have been supported on the carrier, solvent is removed either by vaporation into dryness or filtration. The catalyst is then calcined at a temperature from 400° C. to 700° C., preferably 450° C. to 600° C.

In the sequential impregnation method, the catalyst is prepared by immersing a carrier in an aqueous solution containing a lead compound such as, e.g., lead nitrate and lead chloride, to support the lead component on the carrier, drying the resulting material and then calcining the dried product at a temperature ranging from 300° C. to 800° C. The calcined product is then immersed in an aqueous solution containing a platinum compound such as, e.g., chloroplatinic acid, to support the platinum component thereon, drying the resulting assembly and then calcining the dried product at a temperature ranging from 400° C. to 700° C., preferably from 450° C. to 600° C.

In the simultaneous impregnation method and in the sequential impregnation method mentioned above, amounts of platinum, lead and a third component contained in the solution of platinum compound, lead compound and third component are, in general, 0.01–5 wt. percent platinum; 0.01–5 wt. percent lead and 0–3 wt. percent third component. However, in the simultaneous impregnation method, the ranges preferably are 0.1–1 wt. percent platinum; 0.1–2 wt. percent lead and 0–1 wt. percent third component. On the other hand, in the sequential impregnation method, the ranges preferably are 0.1–1 wt. percent platinum; 0.1–2.5 wt. percent lead and 0–1 wt. percent third component.

Lead to platinum weight ratio in the solution generally ranges from 0.1 to 3.0, and preferably, in the simultaneous impregnation method, it ranges from 0.3 to 2.0, and in the sequential impregnation method, it ranges from 0.3 to 2.5. As with the conventional catalysts, the proportion of contents of the components depends, for example, upon the type of carrier, surface area, order of the addition, method of the calcination and the like.

In order to increase the activity of the catalyst, the use of a carrier such as silica alumina, alumina, alumina hydrate, silica, zeolite, kaolin, acid clay or bentonite is effective and preferable carriers are alumina, silica alumina, zeolite and the like.

The hydrocarbons which may be used in the present invention as the starting material include those mainly comprising paraffins, olefins and naphthenes having a boiling point point within the range of from 40 to 350° C., which may be used alone or in admixture of two or more kinds. Preferable hydrocarbons are those having from 6 to 12 carbon atoms.

Most advantageous materials from the industrial standpoint are naphthas having a boiling range of 40–190° C., kerosene having a boiling range of 160–260° C., and gas oil having a boiling range of 220–350° C.

Feeding ratio of hydrogen to hydrocarbon in gas volume is from 0.5 to 15 and preferably from 2 to 10. Prior to the reaction, the catalyst may be pretreated with hydrogen at or near the reaction temperature to activate it.

Feeding rate of the hydrocarbon in terms of LHSV, which stands for liquid hourly space velocity, (the feeding amount of hydrocarbon per unit time, per unit volume of catalyst, in ml.) is from 0.2 to 10 $hr.^{-1}$ and preferably from 0.5 to 5 $hr.^{-1}$.

Temperatres from 300° C. to 650° C., preferably from 430° C. to 580° C., are employed for the reaction.

The reaction pressure is dependent upon the desired quality of product and economy and may be optionally chosen whithin the range of from 1 to 50 $kg./cm.^2$ and preferably from 5 to 20 $kg./cm.^2$. In order to improve the space time yield in the commercial production, the reaction is preferably carried out under an elevated pressure.

DESCRIPTION OF PREFERRED EMBODIMENTS

In order to illustrate the invention examples are given below.

Example 1

In an aqueous solution of a mixture of chloroplatinic acid and lead chloride was immersed γ-alumina. After being dried, the resulting mass was calcined at 550° C. for 2 hours to prepare a catalyst with a composition: 0.5%Pt-0.25%Pb-Al_2O_3. Percent is by weight herein unless otherwise noted.

Through a catalyst layer containing 20 ml. of the catalyst, which was heated in advance in the presence of hydrogen at 500° C. for 2 hours, was passed a gaseous mixture of hydrogen and n-heptane at a molar ratio of 3:1 at an LHSV of 0.5 hr.$^{-1}$ under atmospheric pressure, while maintaining the layer at a temperature of 490° C. The average molar yields of the products in 10 hours were: Benzene 2.2%, toluene 63.5% and xylenes including ethyl-benzene 2.1% and the total aromatics 67.8%.

Example 2

A hundred milliliters of a catalyst prepared by the same method as in Example 1, the compositions being 0.5%Pt-0.5%Pb-Al_2O_3, was heated under hydrogen at 500° C. for 2 hours. Through the catalyst layer was passed a gaseous mixture of hydrogen and naphtha with the composition given below at a feeding ratio of 3:1 (by gas volume) at an LHSV of 2.0 hr.$^{-1}$ under a total reaction presure of 10 kg./cm.^{2} (gauge) continuously for 48 hours, while maintaining the layer at a temperature of 500° C. Yields by weight of the products were: Hydrogen 4.5%, benzene 5.4%, toluene 15.3%, xylenes 30.6% and the total aromatics 76.7%.

COMPONENT OF THE NAPHTHA SOURCE (PERCENT BY VOLUME)

Paraffins	65.7
Olefins	0
Naphthenes	22.8
Aromatics	11.5

Example 3

The catalyst was prepared by the same method as in Example 1 which had the composition: 0.5%Pt-0.2%Pb-Al_2O_3. The catalyst, 100 ml., was reduced under hydrogen at 530° C. for 1 hour. Then, a gaseous mixture of hydrogen and naphtha with the composition given below at a ratio of 7.5:1 was continuously reacted for 120 hrs. over the catalyst at an LHSV of 2.5 hr.$^{-1}$ and a reaction temperature of 510° C. under a reaction pressure of 9 kg./cm.^{2} (gauge). The research octane number (clear) on average after 120 hrs. was 16.

COMPOSITION OF THE STARTING MATERIAL (PERCENT BY VOLUME)

Paraffins	65.5
Olefins	0.2
Naphthenes	23.7
Aromatics	10.6

Example 4

With 100 cc. of a catalyst composition comprising 0.5% platinum, 0.5 lead and γ-alumina was supported 0.3% potassium carbonate by impregnation and after the catalyst was reduced by hydrogen for an hour at 530° C., a gaseous mixture of hydrogen and naphtha having a composition shown below in a volume ratio of 10:1 was passed therethrough at an LHSV of 1.0 hr.$^{-1}$ at a reaction temperature of 480° C. under a reaction pressure of 4 kg./cm.^{2} (gauge).

COMPOSITION OF THE STARTING NAPHTHA

Ingredient:	Volume percent
Paraffins	65.5
Olefins	0.2
Naphthenes	23.7
Aromatics	10.6

As a result, the yields of the reaction products based on the starting naphtha were as follows:

Catalyst composition: Pt-Pb-K_2CO_3

Reaction time (hr.)	20	100	200
Composition of liquid (wt. percent):			
Benzene	1.9	1.8	1.9
Toluene	11.9	10.5	11.3
Xylene	28.7	25.8	25.7
C_9 aromatics	36.4	33.8	31.8
C_{10} and higher aromatics	9.3	10.8	11.4
Total yield of aromatics	74.3	68.6	68.9

Example 5

γ-Alumina granulated in a ball of a diameter of 2 mm. was immersed in an aqueous solution of rubidium hydroxide, followed by drying and calcination at 570° C. to give a carrier of the composition 0.21% rubidium-99.79% Al_2O_3. The carrier was then immersed in an aqueous solution of a mixture of chloroplatinic acid and lead chloride. After being dried in 2 hours and calcined at 550° C. for 2 hours, there was prepared a catalyst of the composition: 0.5% Pt-0.5% Pb-0.2% Rb-Al_2O_3. A reactor 1.25 inches in diameter was filled with the catalyst and treated under hydrogen for 45 minutes during which period the temperature was raised from 410° C. to 530° C. A gaseous mixture of hydrogen and naphtha with the composition given below in a ratio of 7.5:1 was passed through the reaction tube at an LHSV of 2.0 hr.$^{-1}$ and a temperature of 510° C. under a pressure of 10 kg./cm.^{2}. Yields by weight on average of the products after 25 hrs., on the naphtha basis, were: Benzene 4.4%, toluene 14.9%, xylenes 33.6% and the total aromatics 77.9%.

COMPOSITION OF THE NAPHTHA SOURCE (PERCENT BY VOLUME)

Paraffins	55.2
Olefins	0.1
Naphthenes	31.3
Aromatics	13.4

Example 6

γ-Alumina was immersed in an aqueous solution of a mixture of bismuth nitrate, lead nitrate and chloroplatinic acid, followed by drying and calcination at 530° C. for 4 hours to prepare a catalyst of the composition of 0.4% Pt-0.5% Pb-0.6% Bi-Al_2O_3. Reaction was conducted using 50 ml. of the catalyst under a pressure of 14 kg./cm.^{2} at an LHSV of 2.4 hr.$^{-1}$ for 20 hrs. by the same method as in Example 1. The yields by weight were: Benzene 2.9%, toluene 13.3%, xylenes 29.3% and the total aromatics 71.5%.

Examples 7–27

Twenty milliliters of a catalyst comprising 0.5% platinum, 0.2% lead and a third component were heated at 500° C. for 2 hours in the presence of hydrogen. Through the catalyst layer was passed a gaseous mixture of hydrogen and n-heptane in a molar ratio of 5:1 at an LHSV of 0.5 hr.$^{-1}$ under atmospheric pressure, while maintaining the layer at 510° C. Molar yields of aromatics were as follows:

Example No.	Third component of the catalyst (element	Added amount (percent by weight)	Starting material	Yield of aromatics (molar percent)
7	Li	0.5	LiCl	69.1
8	Na	0.5	Na_2CO_3	68.0
9	Be	1.3	$(BeO)_5 \cdot CO_2 \cdot 5H_2O$	65.1
10	Ca	0.1	$Ca(NO_3)_2 \cdot 4H_2O$	67.6
11	Ba	2.0	$Ba(NO_3)_2$	63.9
12	Zn	0.2	$Zn(NO_3)_2 \cdot 6H_2O$	66.0
13	Cd	0.2	$CdCl_2$	66.8
14	Ge	0.5	Ge*	66.5
15	Sn	0.5	$SnCl_2 \cdot 2H_2O$	75.5
16	Cr	5.3	CrO_3	66.1
17	Mo	1.5	$H_2MO_4 \cdot H_2O$	67.5
18	W	1.5	WCl_3	64.9
19	Re	0.3	$ReCl_3$	65.2
20	Ru	0.05	$RuCl_3$	63.9
21	Rh	0.1	$RhCl_3 \cdot 4H_2O$	65.7
22	Pd	0.3	$PdCl_2 \cdot 2H_2O$	68.0
23	Ir	0.05	$IrCl_4$	64.0
24	Rb Zn	0.1 0.1	$Rb_2SO_4+ZnCl_2$	69.2
25	Ge Sn	0.25 0.25	$GeCl_4$, $SnCl_2 \cdot 2H_2O$	76.4
26	Rb+Zn+Os	0.1+0.1+0.1	Rb_2SO_4, $ZnCl_2OsCl_4$	70.9
27	None			63.7

*Dissolved in HCl.

Example 28

In 200 cc. of an aqueous solution containing 0.0128 mol./liter of chloroplatinic acid and 0.0036–0.0605 mol./

liter of lead nitrate were immersed 140 cc. of γ-alumina having a particle size of 2–3 mm. diameter as a carrier. The resulting product was evaporated to dryness, and then calcined at 550° C. for 3 hours. As shown in Table I, following, compositions of the resulting catalysts are 0.5 wt. percent Pt; 0.15–2.50 wt. percent Pb and Al_2O_3, while Pb/Pt ratio is from 0.3 to 5.0. After 20 cc. of the resulting catalyst were heated at 500° C. in the presence of hydrogen for 2 hours, a mixed gas consisting of hydrogen and n-heptane in a molar ratio of 3:1 was passed through the catalyst layer maintained at 490° C. under atmospheric pressure at a liquid hourly space velocity of 0.5 $hr.^{-1}$. As a result, molar yields of various reaction products were as shown below.

TABLE I

Run number	Concentrations in aqueous solution: Chloroplatinic acid (mol/liter)	Concentrations in aqueous solution: Lead nitrate (mol/liter)	Amount of Pb added wt. (percent)	Pb/Pt ratio (by wt.)	Overall yield of benzene, toluene xylene produced (mol percent)
1	0.0128	0.0036	0.15	0.3	69.5
2	0.0128	0.0060	0.25	0.5	77.2
3	0.0128	0.0121	0.50	1.0	67.8
4	0.0128	0.0314	1.30	2.6	62.6
5	0.0128	0.0362	1.50	3.0	52.0
6 (comparative)	0.0128	0.0605	2.50	5.0	23.1
7 (comparative)	0.0128		0	0	25.3

Example 29

In 200 cc. of an aqueous solution containing 0.0072–0.122 mol./liter of lead nitrate were immersed 140 cc. of γ-alumina having a particle size of 2–3 mm. diameter as a carrier, then, after vaporized to dryness, calcined at 550° C. for 3 hours, and, subsequently, immersed in 200 cc. of an aqueous solution containing 0.007–2.026 mol./liter of chloroplatinic acid, followed by vaporizing to dryness and calcining at 550° C. for 3 hours.

As shown in Table II, following, the resulting catalyst had a composition of 0.3–1.0 wt. percent Pt; 0.3–5.0 wt. percent Pb and Al_2O_3, while Pb/Pt ratio was within the range of 0.5–5.0.

After 10 cc. of the resulting catalyst were heated at 530° C. under a hydrogen stream for 2 hours, a mixed gas consisting of hydrogen and naphtha having a composition shown below in a molar ratio of 7:1 was passed through the catalyst layer maintained at 500° C. under a total reaction pressure of 5 kg./cm.² at a liquid hourly space velocity of 1.5 $hr.^{-1}$. Reaction results after 20 hours of operation are tabulated in Table II.

COMPOSITION OF NAPHTHA (VOL. PERCENT)

Paraffin	65.5
Olefin	0.2
Naphthene	23.7
Aromatics	10.6

B.P. (° C.) 88–189

TABLE II

Run number	Concentration of—: Lead nitrate solution (mol/liter)	Concentration of—: Chloroplatinic acid (mol/liter)	Weight percent: Pt	Weight percent: Pb	Pb/Pt (wt. ratio)	Weight percent: Liquid yield	Weight percent: Overall aromatic yield
1	0.0072	0.0077	0.3	0.3	1.0	86.2	77.4
2	0.0145	0.0077	0.3	0.6	2.0	87.9	71.7
3	0.0214	0.0077	0.3	0.9	3.0	87.0	62.2
4	0.0072	0.015	0.6	0.3	0.5	85.0	75.3
5	0.0145	0.015	0.6	0.6	1.0	85.1	77.0
6	0.029	0.015	0.6	1.2	2.0	87.6	72.0
7	0.043	0.015	0.6	1.8	3.0	87.1	63.5
8 (comparative)	0.058	0.015	0.6	2.4	4.0	87.0	47.2
9	0.024	0.026	1.0	1.0	1.0	83.0	76.0
10	0.049	0.026	1.0	2.0	2.0	85.3	75.6
11	0.073	0.026	1.0	3.0	3.0	86.7	69.1
12 (comparative)	0.122	0.026	1.0	5.0	5.0	87.4	41.5
13 (comparative)		0.0077	0.3			84.1	47.3
14 (comparative)		0.015	0.6			79.0	51.2
15 (comparative)		0.026	1.0			77.9	62.6

Example 30

In 200 cc. of an aqueous solution containing 0.0121 mol./liter of lead chloride were immersed 140 cc. of γ-alumina as a carrier. The resulting product was vaporized to dryness, calcined at 550° C. for 3 hours, and subsequently, immersed in 200 cc. of an aqueous solution containing 0.0128 mol./liter of chloroplatinic acid, followed by vaporizing to dryness and calcining at 550° C. for 3 hours.

The resulting catalyst had a composition of 0.5 wt. percent Pt; 0.5 wt. percent Pb and Al_2O_3, while Pb/Pt ratio is 1.0.

After 20 cc. of the resulting catalyst were heated at 500° C. in the presence of hydrogen for an hour, a mixed gas consisting of hydrogen and n-heptane in a molar ratio of 5:1 was passed through the catalyst layer maintained at 500° C. under atmospheric pressure at a liquid hourly space velocity of 0.5 $hr.^{-1}$.

As a result, the molar yield of total aromatic hydrocarbons produced based on heptane was 78.3%.

Data shown in Tables I and II are also shown graphically in the accompanying Figure.

Comparative Example 1

20 cc. of a known catalyst comprising 0.5% Pt and 99.5% γ-alumina were heated at 500° C. under a hydrogen stream for an hour. Then, there was passed a mixed gas consisting of hydrogen and n-heptane in a molar ratio of 3:1 through the catalyst layer maintained at 500° C. under atmospheric pressure at a liquid hourly space velocity of 0.5 $hr.^{-1}$. As a result, molar yields of the resulting products were as follows:

REACTION PRODUCTS (PERCENT)

Aromatics:	
Benzene	4.5
Toluene	17.6
Xylene	3.1
C_{9+} Aromatics	Trace
Total Aromatics	25.3
C_5–C_7 Paraffins	40.8

Gaseous component:	
Methane	8.5
Ethane	6.7
Propane	6.6
Propylene	0.8
Butane	10.0
Total C_1–C_4	32.6

Due to a drastic decrease in catalyst activity experienced in the instant reaction, the results shown above were values obtained after operation of an hour.

Comparative Example 2

Twenty milliliters of a known catalyst consisting of 0.5% platinum and 99.5% γ-alumina were heated under hydrogen at 500° C. for 1 hour. Through the catalyst layer was passed a gaseous mixture of hydrogen and n-heptane at an LHSV of 0.5 $hr.^{-1}$ under atmospheric pressure, while maintaining the layer at 510° C. Molar yields of the products were: Benzene 8.7%, toluene 36.7%, xylenes 3.8% and the total aromatics 49.2% after a reaction time of 1 hour.

Comparative Example 3

Fifty milliliters of a known catalyst consisting of 0.5% of platinum and 99.5% γ-alumina were heated under hydrogen at 500° C. for 2 hours. Through the catalyst layer was passed a gaseous mixture of hydrogen and naphtha with the composition given below in a ratio of 3:1 at an LHSV of 0.2 $hr.^{-1}$ under atmospheric pressure, while maintaining the layer at 500° C. Yields by weight of the products were: Hydrogen 0.9%, benzene 3.8%, toluene 9.8%, xylenes 8.4% and the total aromatics 28.5% after one hour's reaction.

COMPOSITION OF THE NAPHTHA SOURCE (PERCENT BY VOLUME)

Paraffins	48.3
Olefins	0.4
Naphthenes	38.6
Aromatics	12.7

The catalysts described herein can also be used for conversion of hydrocarbons such as hydrocracking, isomerization and dehydrogenation.

What is claimed is:

1. A catalyst composition comprising from about 0.01 to about 5 weight percent of platinum, from about 0.01 to about 5 weight percent of lead, up to 2.0 weight percent of a halogen, and the balance a carrier, wherein the ratio of lead to platinum is from 0.3 to 2.5, said catalyst being prepared by simultaneously supporting said platinum and lead components on said carrier by impregnation, or first supporting said lead component on said carrier by impregnation and thereafter supporting said platinum component on said carrier by impregnation.

2. A catalyst composition according to Claim 1, wherein a third component selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, berylium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, germanium, bismuth, chromium, molybdenum, tungsten, uranium, rhenium, ruthenium, rhodium, palladium, osmium and iridium, is supported on the carrier in an amount of up to about 3 weight percent.

3. A catalyst composition according to Claim 2, wherein said third component is incorporated before, after or simultaneously at the time of supporting both said platinum and lead components on said carrier.

4. A catalyst composition according to Claim 1, wherein said platinum component is a compound of platinum and halogen.

5. A catalyst composition according to Claim 1, wherein the catalyst contains chlorine in an amount of 0.1–2.0% by weight based on the total weight of catalyst components.

6. A catalyst composition according to Claim 1, wherein said carrier is selected from the group consisting of alumina, alumina hydrate, alumino gel, silica-alumina and a zeolite.

7. A catalyst composition according to Claim 2, wherein said catalyst contains from about 0.1 to about 1 wt. percent platinum, from about 0.1 to about 2 wt. percent lead and from 0 to about 1 wt. percent third component, wherein the ratio of lead to platinum ranges from 0.3 to 2.0, and is prepared by a simultaneous impregnation method.

8. A catalyst composition according to Claim 2, wherein said catalyst contains from about 0.1 to about 1 wt. percent platinum, from about 0.1 to about 2.5 wt. percent lead and from 0 to about 1 wt. percent third component, and is prepared by said sequential impregnation method.

9. The method of preparing a platinum- and lead-containing catalyst composition supported upon a carrier, which comprises:

(a) mixing a carrier with a solution containing platinum and lead ions, and

(b) drying and calcining the dried mixture of (a) at a temperature of from 400° C. to 700° C.,

the amount of platinum and lead present in (a) being from about 0.01 to about 5 weight percent platinum and from about 0.01 to about 5 weight percent lead in a weight ratio of lead to platinum of from 0.3 to 2.5.

10. The method of Claim 8, wherein the solution in (a) is an aqueous solution.

11. The method of Claim 8, wherein the solution in (a) contains a compound of platinum and a compound of lead.

12. The method of Claim 8, wherein there is provided in (a) from about 0.1 to about 1 weight percent platinum and from about 0.1 to about 2 weight percent lead in a weight ratio of lead to platinum of from 0.3 to 2.

13. The method of preparing a platinum- and lead-containing catalyst composition supported upon a carrier, which comprises:

(a) mixing a carrier with a solution containing lead ions,

(b) drying and calcining the dried mixture of (a) at a temperature of from 300° C. to 800° C.,

(c) mixing the calcined composition obtained in (b) with a solution containing platinum ions,

(d) drying and calcining the dried mixture of (c) at a temperature of from 400° C. to 700° C.,

the amount of lead present in (a) and the amount of platinum present in (c) being from about 0.01 to about 5 weight percent and from about 0.01 to about 5 weight percent, respectively, in a weight ratio of lead to platinum of from 0.3 to 2.5.

14. The method of Claim 12, wherein the solutions of (a) and (c) are aqueous solutions.

15. The method of Claim 12, wherein the amount of lead present in (a) and the amount of platinum present in (c) are from about 0.1 to about 1 weight percent and from about 0.1–2.5 weight percent, respectively.

References Cited

UNITED STATES PATENTS

3,425,792	2/1969	Stephens	252—460 X
3,686,340	8/1972	Patrick et al.	252—466 PT X
3,607,728	9/1971	Wilhelm	252—472 X
3,649,565	3/1972	Wilhelm	252—466 PT
3,761,426	9/1973	Wilhelm	252—441 X

DANIEL E. WYMAN, Primary Examiner

P. F. SHAVER, Assistant Examiner

U.S. Cl. X.R.

260—668 D; 252—460, 466 PT, 472