

1

3,366,705

ISOMERIZATION PROCESS

Joseph P. Giannetti, Allison Park, Alfred M. Henke, Springdale, and Raynor T. Sebulsky, Verona, Pa., assignors to Gulf Research & Development Company, a Pittsburgh, Pa., a corporation of Delaware
 No Drawing. Filed June 2, 1965, Ser. No. 460,818
 6 Claims. (Cl. 260-683.68)

Our invention relates to an improved isomerization process whereby relatively unbranched hydrocarbons are isomerized to more highly branched forms.

Processes for isomerizing unbranched hydrocarbons such as, normal paraffins into more highly branched forms such as, isoparaffins, are known to the art. Generally, the suitable feed stocks to such processes as well as the general range of operating conditions of temperature, pressure and space velocity are also well-known in the art. It is an object of our invention to provide an isomerization process substantially improved over those of the prior art.

Our invention includes isomerizing a hydrocarbon feed stock consisting essentially of saturated hydrocarbons by contacting such feed stock with hydrogen under isomerization conditions in the presence of a particular catalyst. The catalyst employed in the process of our invention comprises a minor amount of a metalliferous hydrogenating component composited with a major amount of a carrier comprising alumina and a small quantity of iron combined with the alumina.

We have found that the process of our invention can be conducted at a temperature in the range from about 75° to about 500° F. and preferably from about 150° to about 400° F. while employing a pressure from about 0 to about 3000 p.s.i.g. and preferably from about 0 to about 1000 p.s.i.g. Generally, a liquid hourly space velocity from about 0.1 to about 10.0 and preferably from about 0.5 to 4.0 volumes of feed stock per hour per volume of catalyst can be employed. We have further found that a hydrogen to feed stock molar ratio in the range from about 0.1 to 10.0 and preferably from about 0.1 to 4.0 can be employed in the process of our invention.

The feed stocks suitable for employment in the process of our invention include any hydrocarbon fraction or stock, which is substantially free of olefinic type components and which contains a significant proportion of relatively unbranched saturated components, such as paraffins and naphthenes. It is essential that the feed stock employed in our process does not contain any appreciable amount of olefins since they appear to destroy the effectiveness of our process to isomerize saturated compounds. Our process is effective to isomerize not only completely unbranched saturates, such as normal paraffins, to branched materials, such as isoparaffins, but is also effective to isomerize relatively unbranched hydrocarbons, such as the methylpentanes, to more highly branched forms, such as the dimethylbutanes. Illustrative of sources of such stocks available from various refinery operations are the paraffin rich streams obtained from the raffinate phase of a Udex or Sulfolane process. In the event that such refinery streams contain a significant quantity of olefins it may be necessary to subject them to hydrogenation in order to saturate the olefins prior to charging the material to our process.

The hydrogenating components which can be composited as a minor amount of the total catalyst in our process can be any one of the metals well-known in the art to have hydrogenating activity, such as, for example,

2

Group VI and Group VIII metals. Examples of particularly suitable materials are platinum, iridium, rhodium and palladium. Particularly good results are obtainable with platinum and palladium. Generally, the hydrogenating component can be any one or a mixture of several of the materials mentioned above and can be present in the catalyst in amounts from about 0.01 up to about 5.0 percent by weight based on the total catalyst. Preferably, the metalliferous hydrogenating component comprises from about 0.1 to about 2.0 percent of the total catalyst, particularly in the case of noble metal components.

The alumina of the catalyst carrier of our invention can be any form of porous alumina suitable for use as a catalytic agent or support. For example, excellent results are obtainable with aluminas prepared by calcining a beta-alumina trihydrate such as bayerite or mixtures thereof with other alumina hydrates. Aluminas prepared by calcining other hydrated aluminas, such as, the amorphous alumina formed by hydrolysis of aluminum methoxide, or crystallized alumina hydrates, such as alpha-alumina trihydrate or gibbsite, or naturally occurring materials containing the same, such as bauxite, nordstrandite and alpha- and beta-alumina monohydrate such as boehmite and diaspore or combinations thereof can also be used.

We have unexpectedly found, however, that superior results are obtained in accordance with our isomerization process if a small quantity of iron is combined with the alumina of the carrier. It is essential to the improved processes of our invention that the iron be present in a form combined with the alumina in some chemical or quasicomplex manner and mere physical addition of iron to the alumina base, such as by impregnation, is not satisfactory. Thus, for example, iron can be present in the form of iron aluminate spinel or can be present as some type of a ferric hydroxide or ferric aluminum hydroxide formed during cogellation from a solution of an aluminum salt and a ferric salt. As used throughout the specification and claims the terms combined iron or iron combined with alumina are meant to include chemical or quasicomplex combinations but are meant to exclude strictly physical combinations such as might be obtained by impregnation.

Extremely small quantities of iron combined with the alumina have been found to provide substantial improvement in catalyst activity. Thus, iron is effective when employed in a quantity greater than about 0.5 percent by weight based on the total catalyst. A preferred range for iron is from about 0.5 up to about 5.0 or 6.0 percent. When the iron is combined with the alumina as a spinel, however, an upper limit of about 4.0 percent appears to be the maximum amount desirable.

The alumina carriers employed in the process of our invention can be, aside from the combined iron, essentially pure alumina or they can contain small amounts, up to about 45 percent of other refractory oxides, such as silica, beryllia, titania, zirconia or boria. Such aluminas are usually characterized by a high surface area, generally in the range from about 200 to 500 square meters per gram or more. The carriers employed in our invention can also be promoted with a small amount of a halogen. This halogen promotion can be effected by pre-treating the catalyst with either a pure halogen, an organic halogen compound or an inorganic halogen compound in accordance with any of the techniques well-known in the art. A preferred method of promoting the catalyst employed in our process involves contracting the catalyst with a sulfur chloride at nonreducing conditions

at an elevated temperature, for example in the range of about 200° to 1250° F., preferably from about 500° to about 1100° F. Excellent results are obtainable with thionyl chloride, but other suitable materials are those having the generic formula $S_nO_aX_bY_c$, where S is sulfur, O is oxygen, X is chlorine, Y is a halogen other than chlorine, n is 1 or 2, a is 0, 1, 2, 3 or 5, b is 2 or 4, c is 0 or 1 and the sum of b and c is 2 to 8. Examples of such other materials are sulfur monochloride, sulfur dichloride and sulfonyl chloride. Advantageously, the catalyst composite can be first pretreated with hydrogen and hydrogen chloride at a temperature in the range of about 950° to 1250° F. to improve its susceptibility to activation by contact with a sulfur chloride. In such case the catalyst composite is contacted with the sulfur chloride at nonreducing conditions at an elevated temperature, for example 200° to 1250° F., preferably 300° to 1100° F., effective to promote a substantial increase in the chlorine content of the catalyst. Usually a further enhancement of the catalyst can be effected by a posttreatment subsequent to the sulfur chloride activation mentioned above by treating the catalyst with hydrogen chloride, either with or without hydrogen, at a temperature in the range from about 60° to about 900° F. Especially advantageous results can be obtained when the catalyst is subjected to both the pretreatment and posttreatment along with the sulfur chloride activation.

The catalysts employed in our process can also be promoted by contacting them under nonreducing conditions at an elevated temperature with compounds having the formula



wherein X and Y can be the same or different and are selected from the group consisting of H, Cl, Br, F and SCl and wherein X and Y together can be O or S.

The metalliferous hydrogenating components can be composited with the carrier in any convenient way. Thus, the hydrogenating component can be composited on a precalcined support in the form of an aqueous solution of a water soluble salt followed by drying and calcining the composite. Examples of such solutions are those containing chloroplatinic acid or other halogen platinum acids, or aqueous solutions of nickel and tungsten nitrate. Regardless of the method of compositing the metalliferous component with the catalyst base, the hydrogenating components are advantageously converted to a reduced state prior to the pretreatment with the hydrogen chloride or sulfur chloride in order to minimize loss of the hydrogenating component during sulfur chloride treatment. In the case of base metals such as nickel and tungsten, the hydrogenating component can remain in the form of a sulfide or oxide prior to the hydrogen chloride pretreatment and the sulfur chloride activation treatment. It is, however, important that the hydrogenating component be composited with the carrier before the hydrogen chloride pretreatment and the sulfur chloride activation treatment inasmuch as deposition usually results in a reduction of the chloride content of the treated base.

In order to illustrate our invention in greater detail reference is made to the following examples:

EXAMPLE I

In this example two different catalysts were employed in the isomerization of n-butane to isobutane. In both catalysts the operating conditions employed were the same and included a temperature of 325° F., a pressure of 800 p.s.i.g., a space velocity of 1.0 and a hydrogen to n-butane molar ratio of 2.5 to 1. The first was a commercial catalyst containing 0.6 percent platinum on alumina and generally designated as Sinclair-Baker RD150. The second catalyst comprised 0.35 percent platinum on an alumina base containing 2.0 percent of com-

bined iron as spinel. Carriers of this type are available from Engelhard Industries. Each of the two catalysts were pretreated with hydrogen plus hydrogen chloride at 1050° F. for about 3 hours followed by activation with thionyl chloride at 560° F. for about ¾ to 1 hour and then were posttreated with hydrogen and hydrogen chloride at 400° F. for about 3 hours. The conversions obtained with each of these catalysts is shown in Table I below:

Table I

Catalyst:	Conversion, percent by wt. n-C ₄ converted to iso-C ₄
Commercial cat., 0.6% Pt. -----	47
2.0% Fe as spinel, 0.35% Pt. -----	54

From the above data it will be seen that the catalyst employing a small quantity of iron combined with the alumina support provided a conversion of 54 percent as opposed to only 47 percent conversion obtained with a commercial catalyst. This represents an increase in conversion of about 15 percent in accordance with our invention over that provided by the prior art.

EXAMPLE II

In this example normal butane was again subjected to isomerization at a temperature of 350° F., a pressure of 800 p.s.i.g., a liquid hourly space velocity of 1.0 and a hydrogen to normal butane molar ratio of 2.5 to 1. Three different catalysts were employed in separate runs in this example. One catalyst was the commercial catalyst employed in Example I comprising 0.6 percent platinum on alumina. The second catalyst employed the 0.35 percent platinum on a alumina containing 2 percent iron as spinel described in Example I and the third catalyst was the same commercial catalyst of Example I with 2 percent iron in the form of iron oxide obtained by impregnation. Each of the three catalysts was subjected to pretreatment with hydrogen and hydrogen chloride at 1050° F. for about 3 hours followed by activation with thionyl chloride at 560° F. for about ¾ to 1 hour. The conversions obtained with each of these three catalysts is shown in Table II below:

Table II

Catalyst:	Conversion, percent by wt. n-C ₄ converted to iso-C ₄
Commercial cat. +2% Fe as oxide -----	49
2% Fe as spinel, 0.35 Pt. -----	59
Commercial cat. +2% Fe as oxide -----	49

From the above data it will be seen that when employing a commercial platinum-alumina catalyst with 2 percent iron added by impregnation the conversion obtained is somewhat poorer than that obtained when employing the same plain commercial platinum or alumina catalyst without any iron. On the other hand, however, when 2 percent iron is combined with the alumina in the form of a spinel, the conversion obtained is more than 15 percent greater than that provided by the catalyst supported on an alumina alone and 20 percent greater than the conversion obtained with the same catalyst supported on alumina and impregnated with 2 percent iron. This quite clearly demonstrates that the mere presence of iron alone is not effective to provide the advantageous results of our invention but rather the iron must be combined with the alumina.

EXAMPLE III

In this example a catalyst of the type required in the process of our invention was prepared by forming a first solution containing 4,493 grams of $AlCl_3 \cdot 6H_2O$ in 10 liters of water. A second solution was formed by dissolving 138.5 grams of $AlCl_3 \cdot 6H_2O$ in 2 liters of water and then adding 77.5 grams of $FeCl_3 \cdot 6H_2O$ to the solution and mixing thoroughly. The second solution was then mixed with the first solution. This mixed solution was then added to 5 liters of ammonium hydroxide (28 per-

cent NH_3) in 12.5 liters of water. The aluminum chloride and iron chloride solution was added to the solution of ammonium hydroxide in a slow stream while the pH of the formed slurry was constantly checked. During the course of the addition an additional liter of ammonium hydroxide was added to the mixture in order to maintain the pH above about 9. Upon completion of the addition the pH of the addition mixture was 9.1. The product was filtered and washed with water containing 1 ml. of ammonium hydroxide per liter of water. The washing was stopped when the conductivity of the wash water fell to 12 grains of salt per gallon. The washed material was then dried at 250° F. for 16 hours and sized to 10 to 20 mesh.

A sample of the dried material weighing 416 grams was placed in a small evaporating dish and impregnated with platinum by contacting with 3.0 grams of chloroplatinic acid in 40 ml. of water and mixing thoroughly. The impregnated base was allowed to dry overnight at room temperature followed by calcination in air at 550° F. overnight and then calcination at 900° F. for 2 hours. Analysis of this catalyst indicated that it contained 0.4 percent by weight platinum and 1 percent by weight ferrous iron combined with alumina.

Following the platinum impregnation the catalyst was then pretreated with hydrogen and hydrogen chloride at 1050° F. for about 3 hours followed by activation with thionyl chloride at 560° F. for about ¾ to 1 hour and then it was posttreated with hydrogen and hydrogen chloride at 400° F. for about 3 hours.

This catalyst was then employed in the isomerization of n-butane to isobutane at a temperature of 325° F., a pressure of 800 p.s.i.g., a space velocity of 1.0 and a hydrogen to n-butane molar ratio of 2.5 to 1. Product analysis indicated a conversion of n-butane to isobutane of 53 percent by weight. This example demonstrates that the employment of 1 percent iron combined with the alumina is effective to increase conversion to approximately the same level as that obtained with the catalyst having 2 percent iron as spinel. The conversion obtained with this latter catalyst under the same operating conditions in Example I was 54 percent while in the present example the conversion was 53 percent.

EXAMPLE IV

In this example for catalysts containing the other iron group metals, both impregnated and as spinels, were employed in the isomerization of n-butane to isobutane. The catalysts employed in this example were a 0.6 percent nickel, and a 10 percent nickel both impregnated on the commercial catalyst employed in the preceding examples, a 5 percent nickel combined as spinel with the alumina and a 5 percent cobalt combined with the alumina as spinel plus 0.4 percent platinum. Each of the catalysts of this example was pretreated with hydrogen and hydrogen chloride at 1050° F. for about 3 hours and then activated with thionyl chloride at 560° F. for about ¾ to 1 hour. The reaction conditions employed with all of the catalysts were the same and included a temperature of 350° F., a pressure of 800 p.s.i.g., a space velocity of 1.0 and hydrogen to n-butane molar ratio of 2.5 to 1. The following Table III shows the conversion to isobutane for each of the four catalysts.

Table III

Catalyst:	Conversion, percent by wt. n-C ₄ converted to iso-C ₄
0.6% Ni impregnated	21
10% Ni impregnated	24
5% Ni as spinel with Al ₂ O ₃	20
5% Co as spinel with Al ₂ O ₃ +0.4% pt.	9

It will be noted from the conversions shown in Table III, above, as compared to the conversions obtained in previous examples that the presence of iron group metals other than iron, either impregnated or combined with the

alumina, fails to improve the activity of the catalyst, but rather the presence of nickel and cobalt operates to retard severely the conversion obtained in their absence. This clearly demonstrates that the unexpected capability of promoting isomerization catalysts is not common to all of the iron group meals but is in fact only possessed by iron.

EXAMPLE V

In this example three catalysts were employed in the isomerization of normal butane to isobutane. The first catalyst contained 0.5 percent iron as spinel combined with alumina. The second and third catalysts contained 2.0 percent and 4.0 percent, respectively, iron as spinel combined with alumina. Each of the catalysts was impregnated with 0.35 percent platinum. After impregnation, each catalyst was also pretreated with hydrogen and hydrogen chloride at 1050° F. for about 3 hours followed by activation with thionyl chloride at 560° F. for about ¾ to 1 hour after which the catalysts were posttreated with hydrogen and hydrogen chloride at a temperature of 400° F. for about 3 hours. The operating conditions employed with each of the three catalysts included a temperature of 325° F., a pressure of 800 p.s.i.g., a space velocity of 1.0 and a hydrogen to normal butane molar ratio of 2.5 to 1. The conversion obtained with each of these catalysts is shown in Table IV below.

Table IV

Catalyst:	Conversion, percent by wt. n-C ₄ converted to iso-C ₄
0.5% Fe as spinel—Al ₂ O ₃ +0.35% Pt	45
2.0% Fe as spinel—Al ₂ O ₃ +0.35% Pt	54
4.0% Fe as spinel—Al ₂ O ₃ +0.35% Pt	48

It will be noted from the data in Table IV above that the conversion obtained with 0.5 percent iron as spinel does not provide any increased conversion over that provided by the commercial catalyst in Example I employing the same conditions. It will also be noticed that the employment of 4.0 percent iron as spinel provides a conversion, as shown in Table IV, which is somewhat greater than the commercial platinum-alumina catalyst of Example I. On the other hand, however, the catalyst of the present example employing 2.0 percent iron as spinel provides a conversion about 15 percent greater than that obtained with the other catalysts mentioned. It will be readily seen, therefore, that when employing iron, in accordance with our invention, it is essential that it be employed in an amount greater than 0.5 percent in order to obtain the increased conversion provided by our invention.

We claim:

1. A process for isomerizing a hydrocarbon feed stock consisting essentially of saturated hydrocarbons which comprises contacting the feed stock with hydrogen and a catalyst at a temperature from about 75° to about 500° F., a pressure from about 0 to about 3000 p.s.i.g., a liquid hourly space velocity from about 0.1 to about 10.0 volumes of feed stock per hour per volume of catalyst and a hydrogen to feed stock mole ratio from about 0.1 to about 10.0, said catalyst consisting essentially of from about 0.01 to about 5.0 percent by weight based on the weight of the total catalyst of a metalliferous hydrogenating component selected from the group consisting of Group VI and Group VIII metals composited with a major amount of a carrier comprising alumina and from about 0.5 to about 4.0 percent by weight based on the total catalyst of iron combined with the alumina as a spinel, said catalyst being activated by contacting it with a sulfur compound selected from the group consisting of thionyl chloride, sulfur monochloride, sulfur dichloride and sulfuryl chloride, said contacting step being carried out at nonreducing conditions and at an elevated temperature sufficient to promote a substantial increase in the chlorine content of the catalyst composite.

2. The process of claim 1 wherein the contacting of

7

the catalyst with the sulfur chloride is conducted at a temperature from about 200° to about 1250° F.

3. The process of claim 1 wherein the catalyst is pre-treated with hydrogen and hydrogen chloride at a temperature from about 950° to about 1250° F. prior to activation with the sulfur chloride.

4. The process of claim 1 wherein the catalyst is post-treated with hydrogen chloride at a temperature from about 60° to about 900° F. subsequent to activation with the sulfur chloride.

5. The process of claim 1 wherein the catalyst is pre-treated with hydrogen and hydrogen chloride at a temperature from about 950° to about 1250° F. prior to activation with the sulfur chloride and the catalyst is post-treated with hydrogen chloride at a temperature of about 60° to about 900° F. subsequent to the activation with sulfur chloride.

6. The process of claim 1 wherein the sulfur chloride is thionyl chloride.

8

References Cited

UNITED STATES PATENTS

2,785,138	3/1957	Milliken	-----	252—415
2,900,425	8/1959	Block et al.	-----	260—683.75
3,218,267	11/1965	Goble et al.	-----	260—683.68

OTHER REFERENCES

Remy: Treatise on Inorganic Chemistry, vol. I, pages 355-6, Elsevier Publishing Company, New York.

10 Ladoo et al.: Nonmetallic Minerals, 2nd ed., McGraw-Hill, N.Y., 1951, page 88.

Moeller: Inorganic Chemistry, pages 519-520, John Wiley & Sons, N.Y., 1952.

15 DELBERT E. GANTZ, *Primary Examiner.*

R. H. SHUBERT, G. J. CRASANAKIS,
Assistant Examiners.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,366,705

January 30, 1968.

Joseph P. Giannetti et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 40, "means" should read -- meant --; line 67, "contracting" should read -- contacting --. Column 4, TABLE II, first column, line 1 thereof, cancel "+ 2% Fe as oxide"; same TABLE II, second column, line 1 thereof, "49" should read -- 51 --. Column 5, line 6, "aded" should read -- added --; line 46, "for" should read -- four --. Column 6, line 6, "meals" should read -- metals --.

Signed and sealed this 12th day of August 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents