PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Isomerisation of Paraffin Hydrocarbons

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2., a British joint-stock Corporation, and JOHN NORMAN HARESNAPE and ANTHONY GEORGE GOBLE, both of the Company's Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex and both of British nationality, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the isomerisation of C_4 and higher paraffin hydrocarbons in the gasoline boiling range (i.e. up to 200°C). The term "isomerisation" includes the conversion of normal paraffins to iso-paraffins and also the conversion of iso-paraffins to iso-paraffins with a higher degree of branching.

Catalysts comprising an inorganic oxide, fluorine and a hydrogenating metal are known. For example, catalysts of platinum, alumina and combined halogen are well known as catalysts for the reforming of petroleum naphthas. The amount of halogen may be from 0.1 to 8% wt., although in actual commercial practice, the amount rarely exceeds 1% wt. These catalysts are also suitable for the isomerisation of hydrocarbons at relatively high temperatures and in U.K. Patent Specification No. 823,010 an isomerisation process uses a catalyst comprising alumina, a platinum group metal, from 2.0 to 5.0% by weight of combined fluorine and less than 0.075% by weight of combined chlorine.

It has now been found that the important criterion is not the total weight of fluorine, but the weight of fluorine in relation to the surface area of the alumina.

According to the present invention a process for the isomerisation of C_4 and higher paraffin hydrocarbons in the gasoline boiling range comprises contacting the hydrocarbons in the presence of hydrogen at a temperature of at least 250°C with a catalyst of a platinum group metal, alumina and at least 1% wt. of fluorine, by weight of total catalyst, the fluorine being present in an amount of from 1.2×10^{-4} to 3.4×10^{-4} grams/sq. metre of the original alumina surface area.

The fluorine is believed to be retained on the catalyst by reaction with certain surface groups containing oxygen, particularly hydroxyl groups, originally present on the alumina and the number of these available surface groups is in its turn dependent on the surface area. Each group takes up one or two fluorine atoms and the amount taken up should be such as to give the above relationship between the amount of fluorine and the surface area. With the preferred method of fluorination given later, two fluorine atoms are taken up and an oxygen atom is given up. For maximum fluorination of the available surface groups the amount of fluorine will be of the order of 3.4×10^{-4}, for example 3.0 to 3.4×10^{-4}, the variation being due to possible slight variation of the amount of surface groups per cent of surface area between aluminas prepared in different ways. An amount of fluorine in excess of 3.4×10^{-4} grams/sq. metre of surface area implies either that reaction with the alumina proper is occurring, or that the fluorine is not adequately held on the catalyst and amounts in excess of this amount are, therefore, avoided. Fluorination up to the limit specified results in little or no loss of surface area, for example not more than 10%, but an excess of fluorine results in a greater loss of surface area. Desirably, therefore, there is not more than 10% difference between the surface area of the original alumina and the fluorinated alumina.

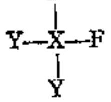
It follows from the above that catalysts with high fluorine contents can be prepared by selecting aluminas of high surface area, and it is possible to use aluminas with a surface area, as measured by low temperature nitrogen absorption using the BET method, of at

[*Price 4s. 6d.*]

least 300 sq. m/gram, and preferably at least 400 sq. m/gram. Such oxides give a preferred fluorine content of at least 5.0% wt. and it may be in excess of 8.0% wt. Having regard to the surface areas of aluminas suitable for use as catalyst supports, the upper limit of fluorine content is likely to be in the region of 15% wt.

Provided the amount of fluorine does not exceed the relationship between fluorine content and surface area given above, it has been found that increase of fluorine content increases the isomerisation activity of the catalyst and decreases its hydrocracking activity giving increased selectivity. This is in contrast to a previous suggestion that isomerisation activity declines at fluorine contents above 5.0% wt.

The fluorine is preferably added to the alumina after the platinum group metal has beed added. If necessary the platinum-alumina composite may be dried and/or calcined before contact with the fluorine. Another suitable source of platinum-alumina composites can be found among the commercially available catalytic reforming catalysts. It may be added in any convenient manner, but a particularly suitable method is that disclosed in copending U.K. Patent Application No. 20525/61 (Serial No. 956,684). This application claims a method for preparing catalysts, which comprises contacting a halogenatable inorganic oxide at elevated temperature with the vapour of a fluorine compound of general formula:



$$\begin{array}{c} F \\ | \\ Y-X-F \\ | \\ Y \end{array}$$

(where X is carbon or sulphur and Y is fluorine or hydrogen) to give a catalyst containing at least 1% wt. of fluorine.

The compounds within the general formula are carbon tetrafluoride, fluoroform, methylene fluoride, and the corresponding sulphur compounds, carbon tetrafluoride being preferred. Carbon tetrafluoride is an extremely stable compound and is not, prima facie, an obvious choice for preparing fluorine containing catalysts. Nevertheless it has been found suitable and it has advantages over other fluorinating compounds. In the particular context of the present invention the method has a particular advantage over the use of hydrogen fluoride, for example, in that high fluorine content catalysts can be prepared without the use of high concentrations of corrosive fluorine compounds which are likely to damage the alumina. The compounds used are also easier to handle and readily utilisable in the vapour phase. As compared with alkyl fluorides containing a higher number of carbon atoms, for example tertiary butyl fluoride, the compounds used are less likely to produce carbonaceous or hydrocarbonaceous deposits in the catalyst during fluorination.

Preferably the contacting of the inorganic oxide with the fluorine compound is carried out under non-reducing conditions. A convenient method of contacting is to pass a stream of the vapour over the alumina either alone or in admixture with an inert gas, for example air. The vapour may be recycled, desirably until all the fluoride has been used, and in this way an accurate control of the amount of fluorine taken up by the catalyst may be obtained.

The temperature, time of contact and amount of fluorine compound used affect the amount of fluorine taken up by the catalyst, increase of any of these increasing the amount taken up. Preferred temperatures are in the range of 300—500°C particularly 350—450°C and the time of contact may be from 5 minutes to 24 hours, particularly 10 minutes to 10 hours. In general higher temperatures are used with lower contact times and vice versa. The amount taken up should not be sufficient to destroy the oxide structures as indicated by X-ray diffraction nor to form detectable amounts of free fluoride or volatile hydrogenating metal-fluorine complexes. As stated earlier, it is believed that the fluorine compound reacts with surface groups of the oxide with loss of an oxygen atom. Thus carbon dioxide is a product of the reaction, and in certain cases, water may also be given off.

The amount of the platinum group metal may be from 0.01 to 5% wt. and preferably from 0.1 to 2% wt. and the preferred platinum group metals are platinum and palladium.

The support should be predominantly alumina but it may, if desired, contain a minor amount by weight of one or more other refractory oxides from Groups III to V of the Periodic Table, for example boria, silica, titania, or zirconia.

The presence of chlorine in the catalyst in amounts up to 1% wt. at least has not been found to be disadvantageous to the activity of the catalyst. However, since chlorine is readily removed from the catalysts at high temperatures and since it competes with fluorine for the available surface hydroxyl sites, the chlorine content is preferably as low as possible, for example below 1% wt.

The feedstock of the process is preferably one containing a major proportion of pentanes, hexanes or a mixture of these paraffins. A feedstock containing a major proportion of hexanes is particularly preferred. If it is desired to isomerise normal paraffins only, the feedstock may first be treated to separate normal paraffins from the other hydrocarbons and the normal paraffins contacted with the isomerisation catalyst. Such separation may conveniently be effected by means of the so-called molecular sieves.

The product of the isomerisation reaction may similarly be treated to recover unconverted normal paraffins which may be recycled, to the isomerisation reaction zone. Such separation may also conveniently be affected by means of the so-called molecular sieves.

The isomerisation is carried out in the presence of hydrogen and the process conditions should be selected to minimise the amount of cracking to lower-boiling material. Such cracking is minimised, for example by the use of lower temperatures, and higher space velocities and the conditions may be selected from the following ranges:

Temperature		250° to 500°, preferably 300 to 400°C
Pressure	psig	atmospheric-2000, preferably 225-1000
Space Velocity	v/v/hr	0.05-10, preferably 0.2-5
Hydrogen/Hydrocarbon mole rate		0.01-20:1, preferably 1.5-15:1

The invention is illustrated by the following examples.

EXAMPLE 1

10 ml of a commercial reforming catalyst consisting of 0.58% wt. platinum and 0.81% wt chlorine supported on alumina and having a specific surface area of 354 m^2/g was contacted with a stream of dry carbon tetrafluoride vapour. The temperature was 450°C, the flow rate 20 ml CF_4/min and the time of contact 30 minutes. The uptake of fluorine was 7.6% wt. (i.e. 2.14 × 10^{-4} grams/sq. metre of surface area).

A sample of the catalyst prepared as above was used to isomerise pure *n*-hexane at 300°C, atmospheric pressure and a hydrogen/*n*-hexane mole ratio of 6.2:1. The results obtained at various gas space velocities were:—

Product % wt	Gas Space Velocity v/v/hr		
	57	129	231
C_1-C_5 hydrocarbons	8.8	3.3	1.6
Total *n*-C_6 isomerised	70.7	73.3	68.2
2,2-dimethylbutane	8.7	6.3	3.5

The non-fluorinated reforming catalyst used as the starting material for the catalyst had a negligible isomerisation activity under the conditions used.

EXAMPLE 2

200 ml of the commercial platinum-on-alumina catalyst used in Example 1 was contacted with a stream of dry carbon tetrafluoride vapour at 460°C. The flow rate was 12 litres/hr and the time of contact was 30 minutes. The uptake of fluorine was 9.3 per cent weight (i.e. 2.63 × 10^{-4} grams/sq. metre of surface area).

A sample of the catalyst prepared above was used to isomerise pure *n*-hexane at 300°C, atmospheric pressure and a hydrogen to *n*-hexane molar ratio of 6.2:1. The results obtained at various gas space velocities were:—

Product % wt	Gas Space Velocity v/v/hr			
	107	146	321	496
C_1-C_5 hydrocarbons	5.4	5.3	2.8	1.4
Total *n*-C_6 isomerised	74.0	74.3	73.6	75.6
2,2-dimethylbutane	13.0	11.3	8.0	5.0

EXAMPLE 3

10 ml of the commercial platinum-on-

alumina catalyst used in Example 1 was reacted at 450°C for 10 minutes with a stream of dry air (2 volumes) and carbon tetrafluoride (3 volumes), flowing at 100 ml/min. The catalyst was then used for the isomerisation of *n*-hexane at atmospheric pressure and hydrogen to *n*-hexane molar ratio of 6.2:1. At 300°C and gas space velocity 46 v/v/hr the product contained 14.0 per cent weight of 2,2-dimethylbutane which, allowing for hydrocracked products, corresponds to a greater than 90 per cent approach to equilibrium.

Another catalyst sample, prepared at the higher temperature of 550°C with the air/CF_4 mixture, gave only 0.3 per cent weight of 2,2-dimethylbutane under similar reaction conditions.

EXAMPLE 4

This example compares the isomerisation activity of catalysts of different surface areas and fluorine contents.

Portions of two commercially available platinum-alumina reforming catalysts were fluorinated to different fluorine contents using a fluorination technique similar to that described in Example 1. The catalysts were of similar composition but had different surface areas as follows:

		Catalyst 1	Catalyst 2
Platinum	% wt	0.58	0.7
Fluorine	% wt	—	0.35
Chlorine	% wt	0.8	0.35
BET surface area	m^2/g	400	180

Portions of the two catalysts were each fluorinated to give different levels of fluorine content and the resultant fluorinated catalysts were used to isomerise *n*-hexane.

The fluorine contents of the catalysts by total weight, and by weight per unit of surface area are given in the tables below, together with the isomerisation conditions used and the results obtained.

Fig. 1 shows the conversion to 2,2-dimethylbutane and the selectivity for isomerisation

CATALYST 1

Isomerisation activity of CF_4 — Treated platinum-on-alumina catalyst (BET 400 m^2/g)

Temperature	300°C
Pressure	atmospheric
Hydrogen : n-hexane mole ratio	6.2:1
GHSV	172 v/v/hr

Fluorine Content % wt	1.3	3.4	6.1	8.0	9.0
BET Surface Area m^2/g	405	402	Not determined	397	393
Fluorine per unit BET surface area 10^{-4} g/m^2	0.33	0.85	1.52	2.00	2.25
Total Conversion of n-C_6 % wt	60.0	79.8	80.5	80.1	81.3
22 dimethylbutane % wt	nil	10.9	13.2	13.7	14.4
Total Isomerisation % wt	15.9	57.8	68.3	70.0	72.8
Hydrocracking (C_1-C_5) % wt	44.1	21.0	12.2	10.1	8.5
Selectivity for Isomerisation %	26.5	72.4	84.8	87.5	89.5

CATALYST 2

Isomerisation activity of CF_4 — Treated platinum-on-alumina catalyst (BET 180 m^2/g)

Temperature	300°C
Pressure	atmospheric
Hydrogen : n-hexane mole ratio	6.2:1
GHSV	172 v/v/hr

Fluorine content % wt	1.1	2.4	3.7	4.6	5.6
BET Surface Area m^2/g	184	186	176	178	178
Fluorine per unit BET surface area 10^{-4} g/m^2	0.61	1.33	2.07	2.55	3.11
Total Conversion of n-C_6 % wt	88.7	78.9	77.7	79.3	79.5
22 Dimethylbutane % wt	5.2	9.8	12.1	15.2	15.0
Total Isomerisation % wt	27.3	59.2	65.4	73.5	74.6
Hydrocracking % wt	61.4	19.7	12.3	5.8	4.9
Selectivity for Isomerisation %	30.8	75.0	84.2	92.7	93.8

The results given in the two tables are shown graphically in Figures 1 and 2 of the accompanying drawings.

plotted against the catalyst fluorine content in % wt. Fig. 2 shows the same isomerisation results plotted against the catalyst fluorine content per unit of surface area.

From Fig. 1 it appears at first sight that cataylst 2 with a surface area of 180 m^2/g is the better isomerisation catalyst. However, Figure 2 shows that at the same fluorine contents per unit of surface area the catalysts have the same activity and that this is the correct criterion to take in assessing catalyst activity.

WHAT WE CLAIM IS:—

1. A process for the isomerisation of C_4 and higher paraffin hydrocarbons in the gasoline boiling range comprising contacting the hydrocarbons in the presence of hydrogen at a temperature of at least 250°C with a catalyst of a platinum group metal, alumina, and at least 1% wt. of fluorine by. weight of total catalyst, the fluorine being present in an amount from 1.2×10^{-4} to 3.4×10^{-4} grams/sq. metre of the alumina surface area.

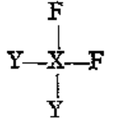
2. A process as claimed in claim 1 wherein the amount of fluorine is from 3.0×10^{-4} to 3.4×10^{-4} gms/sq. metre.

3. A procees as claimed in claim 1 or 2 wherein the alumina surface area is at least 300 sq. metres/gram.

4. A process as claimed in claim 3 wherein the alumina surface area is at least 400 sq. metres/gram.

5. A process as claimed in any of claims 1 to 4 wherein the catalyst is prepared by adding fluorine to a platinum-alumina composite.

6. A process as claimed in any of claims 1 to 5 wherein the catalyst is prepared by contacting the alumina with the vapour of a fluorine compound of general formula



$$Y{-}\overset{\displaystyle F}{\underset{\displaystyle Y}{X}}{-}F$$

(where X is carbon or sulphur and Y is fluorine or hydrogen).

7. A process as claimed in claim 6 wherein the fluorine compound is carbon tetrafluoride.

8. A process as claimed in any of claims 1 to 7 wherein the isomerisation temperature is from 250 to 500°C.

9. A process as claimed in claim 8 wherein the isomerisation temperature is from 300 to 400°C.

10. A process as claimed in any of claims 1 to 9 wherein the pressure is from atmospheric to 2000 psig. the space velocity from 0.05 to 10 v/v/hr and the hydrogen/hydrocarbon mole ratio from 0.01 to 20:1.

11. A process as claimed in claim 10

wherein the pressure is from 225—1000 psig, the space velocity from 0.2—5 v/v/hr and the hydrogen/hydrocarbon mole ratio from 1.5 to 15:1.

12. A process as claimed in claim 1 substantially as described in the Examples.

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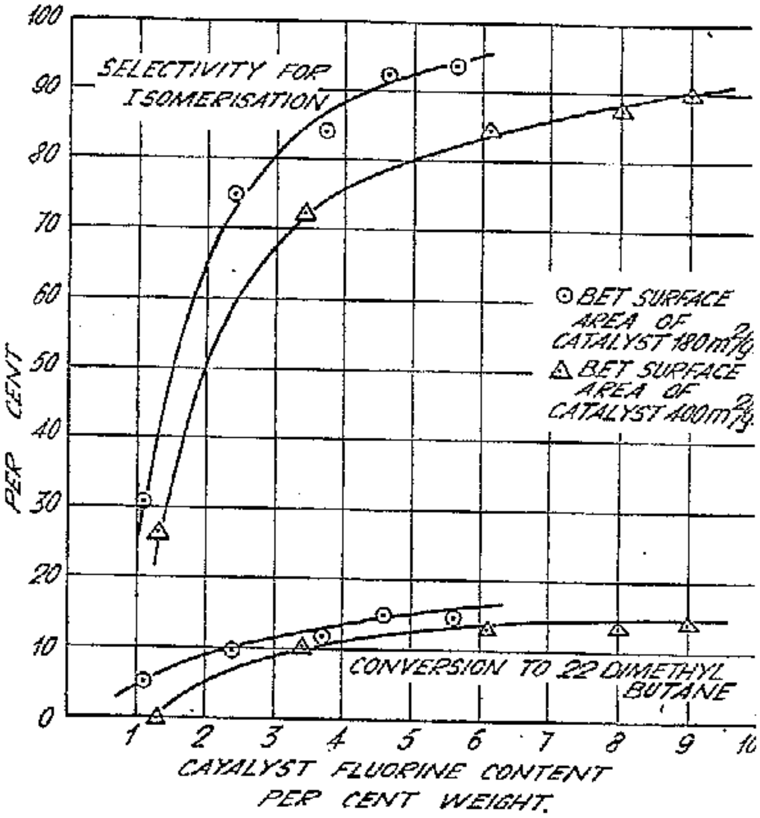
FIG.1.


SELECTIVITY FOR ISOMERISATION
⊙ BET SURFACE AREA OF CATALYST 180m²/g
△ BET SURFACE AREA OF CATALYST 400m²/g
CONVERSION TO 22 DIMETHYL BUTANE
PER CENT
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
CAYALYST FLUORINE CONTENT PER CENT WEIGHT.

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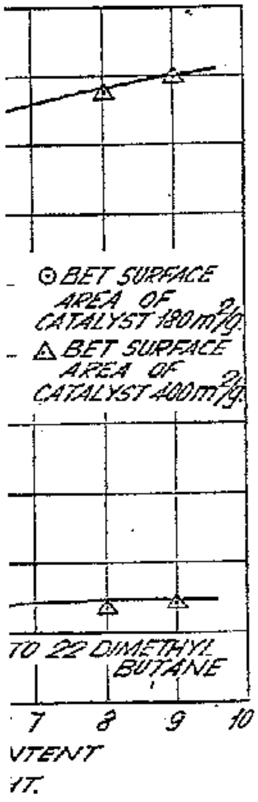
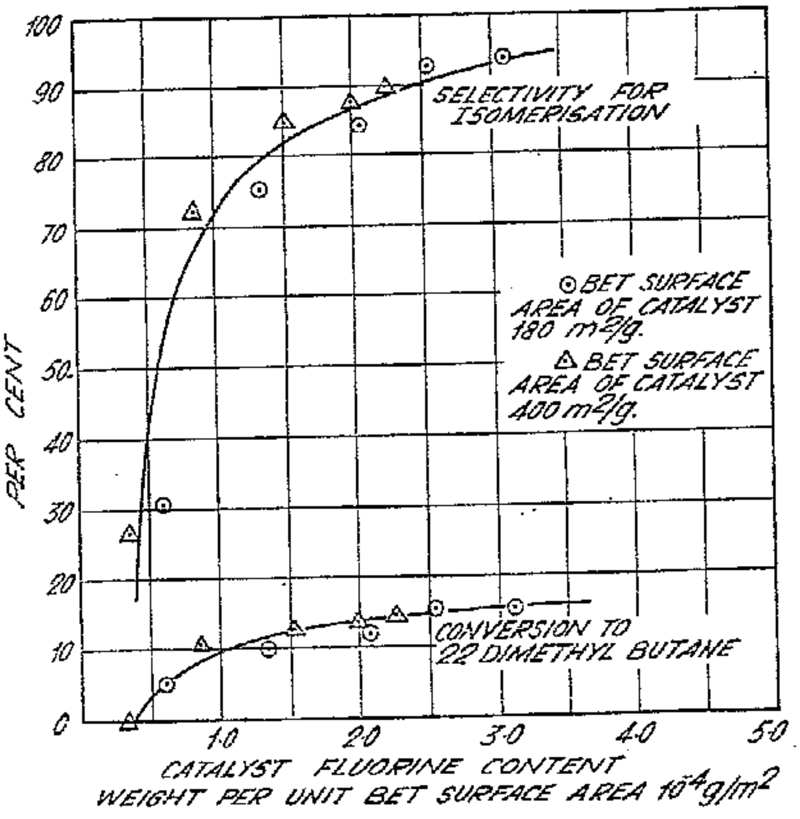
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 1 & 2

FIG.2.





956685 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 1 & 2

FIG.1.

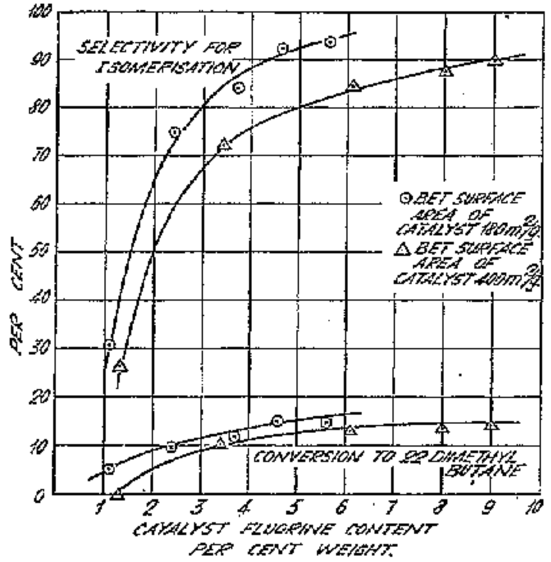


FIG.2.