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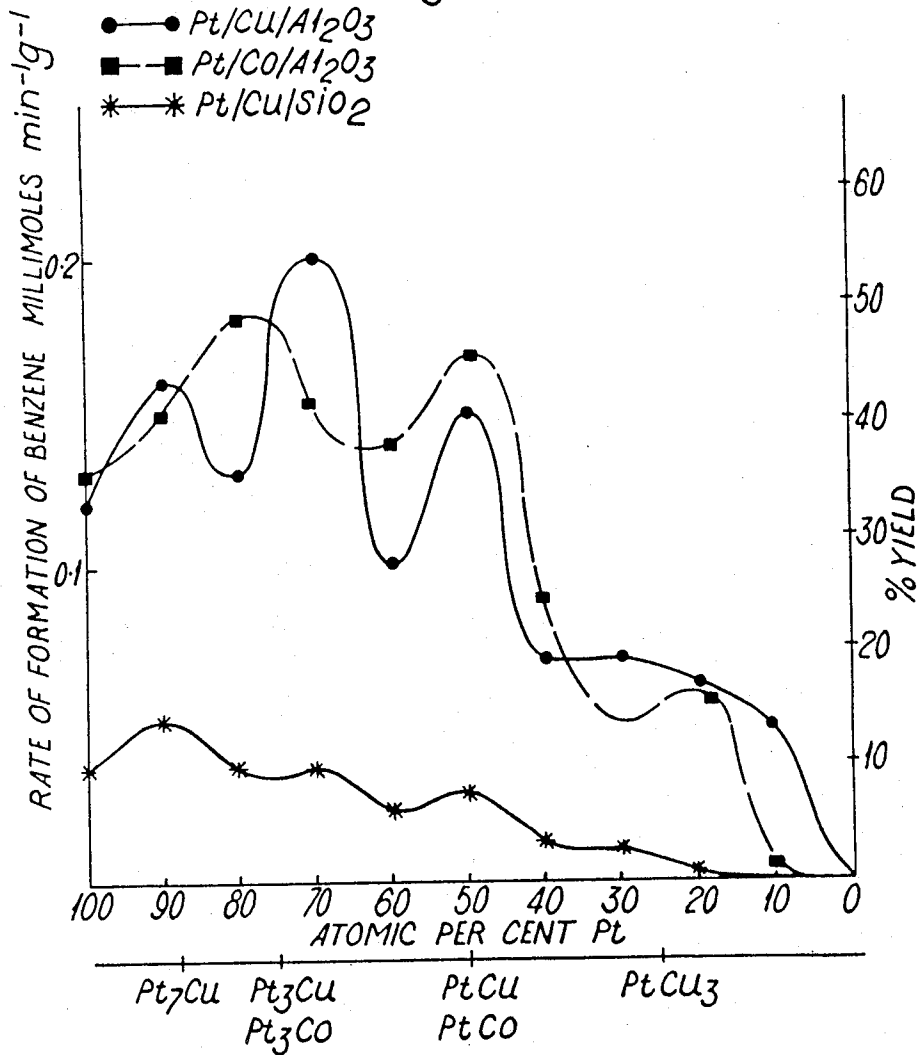
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HYDROCARBON CONVERSION WITH PLATINUM-SECOND-METAL CATALYSTS  
IN PROPORTIONS WHICH FORM ORDERED ALLOYS

Filed March 30, 1971

2 Sheets-Sheet 1

Fig. 1.



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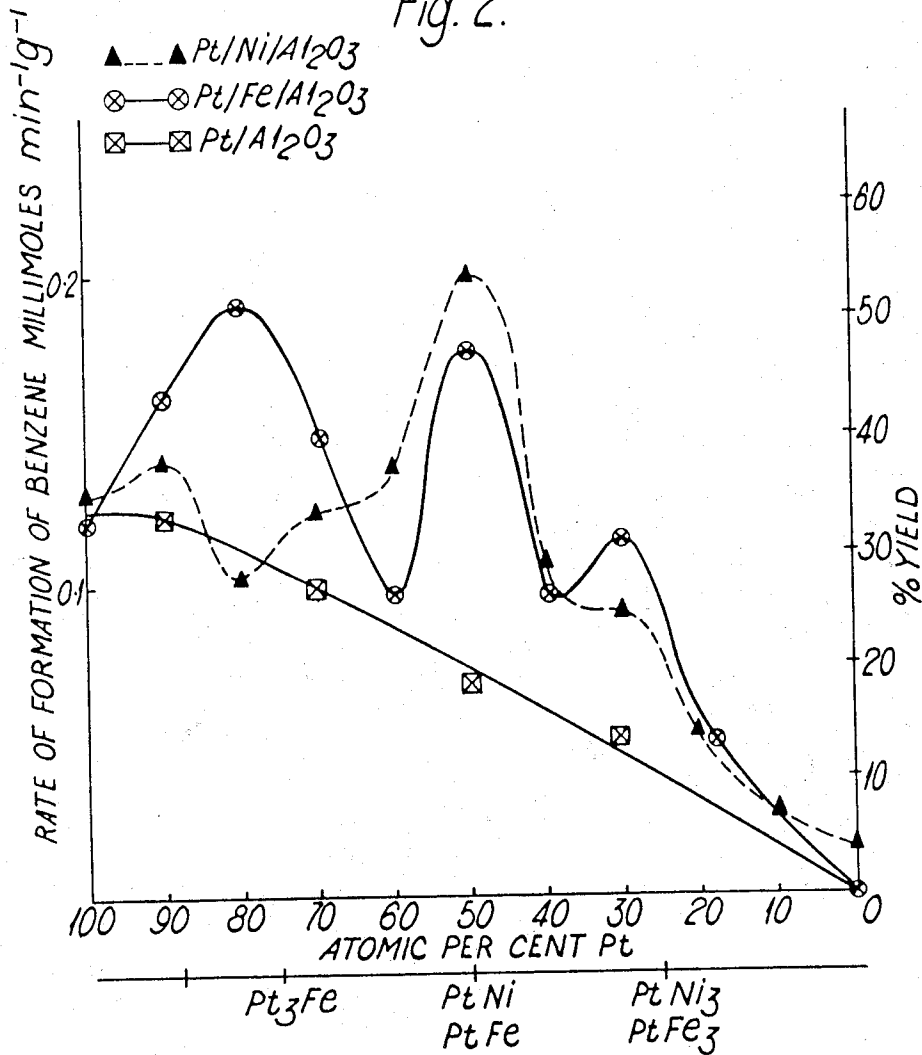
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2 Sheets-Sheet 2

Fig. 2.



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## HYDROCARBON CONVERSION WITH PLATINUM-SECOND-METAL CATALYSTS IN PROPORTIONS WHICH FORM ORDERED ALLOYS

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5 Claims

### ABSTRACT OF THE DISCLOSURE

A hydrocarbon conversion catalyst of 0.01-10% wt. metal on a refractory support contains platinum and a second metal which forms a solid solution with Pt, the atomic amounts of each being equivalent to amounts forming ordered alloy structures. The second metal may be Co, Ni, Fe, Cu, Sn, Pd (particularly these six), Ir, Rh, Ag, Au, Bi, Hg, Sb, Pd or Cd and preferably there is at least 45 atomic percent Pt. The catalysts may be prepared by known impregnation or ion-exchange techniques and are preferably reduced before use at 250-600° C.

The preferred use is dehydrocyclisation or dehydrogenation of C<sub>3</sub>-C<sub>25</sub> hydrocarbons, particularly the catalytic reforming of 15-204° C. boiling range petroleum fractions.

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According to the present invention, therefore, a catalyst suitable for the conversion of hydrocarbons comprising from 0.01 to 10% wt. of metal on a refractory support is characterised in that it contains platinum and a second metal which forms a solid solution with platinum, the atomic amounts of the platinum and the second metal being substantially equivalent to amounts which form ordered alloy structures.

The metallurgy of platinum alloys is well established and metals known to form solid solutions with platinum include cobalt, nickel, iron, copper, tin, palladium, iridium, rhodium, silver, gold, bismuth, mercury, antimony, lead, and cadmium. In accordance with established metallurgical principles the existence of ordered structures in any bi-metallic system can be readily determined, and many of them are already known. These ordered structures have atomic proportions of the two metals in a simple ratio. The ratios may vary with different metals but for any two metals there will be relatively few ordered structures, usually 5 at the most. The most common are

- AB i.e. 50 atomic percent A, 50 atomic percent B
- A<sub>3</sub>B i.e. 75 atomic percent A, 25 atomic percent B
- A<sub>7</sub>B i.e. 87½ atomic percent A, 12½ atomic percent B

Others which may exist in certain systems are A<sub>3</sub>B<sub>2</sub> and A<sub>4</sub>B but, in any system, they can, as indicated above, be detected by standard techniques.

With the second metals listed above the following proportions of platinum and the second metal are known to give ordered structures

Pt <sub>7</sub> Cu	Pt <sub>3</sub> Co	PtCo		PtCo <sub>3</sub>	
Pt <sub>7</sub> Sn	Pt <sub>3</sub> Fe	PtNi		PtNi <sub>3</sub>	
Pt <sub>7</sub> Pd	Pt <sub>3</sub> Cu	PtFe		PtFe <sub>3</sub>	
	Pt <sub>3</sub> Sn	PtCu	Pt <sub>2</sub> Sn <sub>3</sub>	PtSn <sub>3</sub>	PtSn <sub>4</sub>
	Pt <sub>3</sub> Ag	PtSn			
		PtPd			
		PtAg			
		PtBi		PtAg <sub>3</sub>	
		PtHg		PtAu <sub>3</sub>	
		PtSb		PtBi <sub>3</sub>	
Pt <sub>4</sub> Sb	Pt <sub>3</sub> Sb <sub>3</sub>	PtSb			PtHg <sub>4</sub>
	Pt <sub>3</sub> Pb	PtPb			PtPb <sub>4</sub>
	Pt <sub>3</sub> Cd			PtCd <sub>2</sub>	PtCd <sub>3</sub>

This invention relates to platinum-containing catalysts and their use for the catalytic conversion of hydrocarbons.

Catalysts of platinum on a refractory support are well known. The platinum, which may be present in an amount of 0.1 to 5% wt., has good activity for hydrogenation or dehydrogenation and dehydrocyclisation depending on the process conditions. By a suitable choice of support, additional functions of e.g. isomerisation and cracking can be given to the catalyst.

Since platinum is an expensive metal, methods of reducing the platinum content of such catalysts without affecting their performance are potentially useful, and considerable interest has been shown recently in the development of bi-metallic catalysts. It has now been found that both the nature of the second metal and the proportion of this metal in relation to the platinum are important. In particular, it has been found that graphs of catalyst activity against the amounts of metals show distinct peaks corresponding with particular compositions.

The ordered structures Pt<sub>7</sub>Sn and PtCo<sub>3</sub> have not been previously reported but their existence may be presumed from results described hereafter. There is published evidence for the existence of ordered platinum-palladium structures at about Pt<sub>7</sub>Pd and PtPd but their exact composition is less clear. The possibility of ordered structures from platinum-iridium and platinum-rhodium alloys exists but the published evidence is not conclusive.

The term "substantially equivalent to amounts which form ordered alloy structures" means ± 5 atomic percent for each metal.

Preferably the platinum is substantially equal to or greater than the amount of the other metal. The platinum is preferably thus at least 45 atomic percent. The preferred second metals are cobalt, nickel, iron, copper, tin and palladium.

According to another aspect of the invention method of preparing a catalyst suitable for the conversion of hydrocarbons comprising from 0.01 to 10% wt. of metal on a refractory support comprises contacting the support

with a solution containing platinum ions and a solution containing ions of a second metal which forms a solid solution with platinum, the concentration of ions in the solutions and the conditions of contacting being such that the amounts of platinum and the second metal on the catalyst are substantially equivalent to amounts which form ordered alloy structures.

The support may be contacted simultaneously with solutions containing ions of platinum and the second metal or sequentially in either order. Preferably the contacting is carried out sequentially with the platinum containing solution being used first.

The platinum and the second metal may be added by ion-exchange, this being a known term indicating that the ions combine chemically with active sites on the surface of the support. Particularly in the case of supports having few or weak active sites, the support should be washed exhaustively with water while the ions are still in a water-soluble state until the wash water is free of metal ions. This washing ensures that the only metal remaining on the support is in ion-exchanged form. The platinum and the second metal ions can be added in either cation or anion form, the former being preferred since the most commonly used supports are cation-exchangers.

The platinum and the second metal may also be added by impregnation in conventional manner and this is, in fact, preferred.

The term metal ions includes complex ions where the metal is attached to a ligand, particularly water, ammonium, or halogen. Such complex ions are the usual form of ions for many metals in aqueous or ammoniacal solution. Thus the normal platinum containing solutions used in catalyst preparations are tetrammine platinous chloride giving tetrammine platinous cations and chloroplatinic acid giving hexachloroplatinate anions. The second metal solution may contain any suitable salt, e.g. chloride, nitrate, or acetate and may again be an ammoniacal solution.

The conditions of the contacting with platinum and the second metal ions—the temperature, time and concentration of ion in solution—will depend on the ease of uptake and the desired uptake, and may be readily determined by experiment if necessary. Suitable conditions have been found to include temperatures of 10–110° C., times of 1 to 72 hours and solution concentrations of 0.001 to 2 molar.

When preparing ion-exchanged catalysts, the washing to remove uncombined ions desirably uses de-ionised water and, as indicated above, is continued until the wash water is free of ions of platinum and the second metal. The temperature may also be 10 to 110° C., and the time 1 to 72 hours using, preferably, 2 to 100 ml. of water/ml. of catalyst.

The refractory support is preferably an inorganic oxide of an element of Groups II, III and IV of the Periodic Table, a mixture of two or more such oxides or a compound containing one or more of such oxides in its empirical formula. Preferred individual oxides are silica or alumina, preferred mixed oxides are silica-alumina, silica-magnesia, or boria-alumina, and preferred minerals are aluminosilicates e.g. zeolites.

The catalysts may also contain from 0.1 to 8% wt. of halogen, particularly chlorine.

After the addition of the metals the catalyst may be dried e.g. at 50–110° C. for 1 to 24 hours, and calcined at 250 to 600° C. for 1 to 24 hours. Desirably the catalysts are also reduced before use by heating them in a reducing atmosphere at 200 to 600° C. for 1 to 24 hours. The reducing atmosphere is preferably a flowing stream of hydrogen. The reduction of the dual-metal catalyst may be more difficult than that of catalysts containing only platinum and care should be exercised to ensure reduction. The extent of reduction can be monitored by hydrogen uptake from a closed system in which hydrogen is circulated over the catalyst.

The present invention includes a process for the catalytic conversion of hydrocarbons comprising contacting the hydrocarbons under conversion conditions with a catalyst containing platinum and a second metal on a refractory support having a composition as previously described.

Conversion conditions can vary widely depending on the feedstock and reaction but they are normally within the ranges

10 Temperature -----° C. 0–600  
 Pressure -----p.s.i.g. 0–3000  
 Space velocity -----v./v./hr. 0.1–20  
 Hydrogen:hydrocarbon mole ratio ----- 0–20:1

15 The preferred hydrocarbon feedstocks may be derived from any convenient source e.g. from petroleum and their precise nature will depend on the reaction required.

For dehydrogenation and dehydrocyclisation the preferred hydrocarbons are paraffins and/or olefins and/or naphthenes, particularly those having from 3 to 25 carbon atoms. The preferred dehydrogenation or dehydrocyclisation reactions may be operated under the following ranges of conditions:

25 Temperature -----° C. 300–600  
 Pressure -----p.s.i.g. 0–1000  
 Space velocity -----v./v./hr. 0.1–10  
 Hydrogen:hydrocarbon mole ratio ----- 0–20:1

30 Thus the catalysts of the present invention may be used for the catalytic reforming of hydrocarbons boiling in the gasoline range (15 to 204° C.), particularly petroleum fractions, to increase the aromatic content and/or octane number. The preferred support for such use is alumina, possibly containing from 0.1 to 8% wt. of halogen, such a support having the moderate isomerisation and cracking activity usually considered desirable in catalytic reforming.

For hydrogenation reactions the feedstocks may be unsaturated hydrocarbons e.g. acetylenes, olefins, or aromatics, particularly those having from 2 to 20 carbon atoms. The process conditions may be chosen from:

45 Temperature -----° C. 0–300  
 Pressure -----p.s.i.g. 0–2000  
 Space velocity -----v./v./hr. 0.1–20  
 Hydrogen:hydrocarbon mole ratio ----- 0.001 to 20:1

For hydrogenation reactions the catalyst support is preferably relatively inert and may be for example silica, sepiolite or low-acidity alumina.

The invention is illustrated by the following examples.

#### EXAMPLE 1

A series of platinum-copper catalysts was prepared. The support used was silica of 30–60 B.S.S. mesh obtained from Hopkins and Williams Ltd. having a surface area of 170 m.<sup>2</sup>/g. It was freed from iron impurities by washing with normal HCl and distilled water. A catalyst containing 1.8% wt. platinum was prepared by contacting 100 g. silica with 9.22 ml. of a molar solution of tetrammine platinous chloride at 25° C. for 2 h. The silica was then washed with 50 ml. aliquots of deionised water at 25° C. The final wash water was free of platinum ions. The catalyst was dried at 110° C. for 24 hours.

A series of platinum and copper catalysts was prepared by progressively reducing the concentration of tetrammine platinous chloride in the solution and contacting the Pt-SiO<sub>2</sub> with solutions of cupric chloride in 0.880 S.G. aqueous ammonia of progressively increasing concentration. The relative concentrations were adjusted so that each catalyst had the same gram atom metal content as the 1.8% wt. Pt. on silica but varying atomic ratios of Pt and Cu, 90:10, 80:20, 70:30 and so on. In the final catalyst the contacting with platinum was omitted altogether giving a catalyst of 0.59% wt. copper on silica.

75 Washing and drying after each contacting with copper

solution was carried out as for the contacting with platinum solution.

Each catalyst was dried at 110° C. for 24 hours and reduced in 4000 v./v./hr. of hydrogen at 500° C. for 3 hours. Examination by electron spin resonance and measurement of the hydrogen uptake during reduction confirmed that the metal had been reduced. Each catalyst

tested for dehydrocyclisation activity using the n-hexane feedstock and process conditions of Example 1 (i.e. 500° C., atmospheric pressure, 4000 v./v./hr. of feedstock having a 10:1 H<sub>2</sub>:n-hexane mole ratio).

The results obtained are shown in Table 2 below, expressed as conversion rates in millimoles, min.<sup>-1</sup>, gram<sup>-1</sup>.

TABLE 2.—PLATINUM-COPPER-ALUMINA

Atomic percent Pt	Total conversion	Conversion to benzene	Selectivity for benzene, percent	Conversion to toluene	Selectivity for toluene, percent	Conversion to xylenes	Selectivity for xylenes, percent	Total conversion to aromatics	Selectivity for total aromatics, percent
100	0.25	0.11	44.2	0.02	7.3	0.02	4.8	0.13	51.5
90	0.33	0.16	49.5	0.03	7.5	0.02	4.8	0.21	61.8
80	0.25	0.13	51.6	0.02	8.9	0.03	10	0.18	70.5
70	0.27	0.20	73.4	0.03	9.3	0.03	12.3	0.26	95
60	0.16	0.11	65.0	0.01	6.4	0.01	6.8	0.13	78.2
50	0.30	0.15	51	0.02	8.5	0.04	12.9	0.21	72.5
40	0.21	0.07	33	0.01	9.5	0.02	9.5	0.11	52
30	0.17	0.07	41	0.01	5.9	0.02	11.8	0.10	58.7
20	0.17	0.06	35	0.01	5.9	0.03	11.8	0.09	52.7
10	0.12	0.05	42	0.01	8.3	0.03	25	0.09	75.3
0	0.04	Trace	Trace	Trace	Trace	Trace	Trace	0.22	58

was used to dehydrogenate and dehydrocyclise n-hexane at 500° C. and atmospheric pressure. The feedstock of hydrogen and n-hexane (10:1 H<sub>2</sub>:n-hexane mole ratio) was fed in at 4000 v./v./hr.

The results are shown in Table 1 below expressed as conversion rates in millimoles, min.<sup>-1</sup>, gram<sup>-1</sup> × 10<sup>2</sup>.

TABLE 1

Atomic percent Pt in catalyst	millimoles min. <sup>-1</sup> g. <sup>-1</sup> × 10 <sup>2</sup>	
	Total conversion	Conversion to benzene
100	13.3	3.4
90	18.0	5.1
80	14.2	3.7
70	12.8	3.7
60	7.8	2.3
50	13.3	2.7
40	12.8	1.2
30	5.6	1.2
20	9.4	0.3
10	3.6	.1
0	0	0

The conversion products other than benzene were mainly hexenes and coke.

## EXAMPLE 2

Alumina, obtained by calcination of an alumina hydrate precursor in which the trihydrates predominated, having a

TABLE 3.—PLATINUM-COBALT-ALUMINA

Atomic percent Pt	Rate of formation, millimoles min. <sup>-1</sup> gm. <sup>-1</sup>			Selectivity				Total conversion, millimoles min. <sup>-1</sup> gm. <sup>-1</sup>
	Benzene	Toluene	Xylenes	Benzene	Toluene	Xylenes	Total aromatics	
100	0.13	.015	.018	46.5	5.2	6.3	58.0	0.28
90	0.15	.014	.019	58	5.5	7.4	70.9	0.26
80	0.18	.017	.024	64.5	6.2	8.7	79.4	0.28
70	0.15	.015	.026	58	5.8	10	73.8	0.26
60	0.14	.014	.020	61	5.9	8.6	75.5	0.23
50	0.17	.016	.027	68	6.3	10.8	85.1	0.25
40	0.09	.013	.017	39	5.6	7.5	43.1	0.23
30	0.05	.008	.028	27.8	4.5	15	47.3	0.18
20	0.06	.013	.038	35	7.8	22.4	65.2	0.17
10	.003	-----	.009	10	-----	30	40	0.03
0	-----	-----	-----	-----	-----	-----	-----	.004

surface area of 242 m.<sup>2</sup>/g., a pore volume of 0.37 ml./g., and a particle size of 60 to 80 BSS mesh was impregnated with sufficient chloroplatinic acid to give a catalyst containing 0.6 wt. platinum. A series of platinum and copper catalysts was also prepared in a manner similar to Example 1 by progressively reducing the amount of platinum added and impregnating the Pt-Al<sub>2</sub>O<sub>3</sub> with cupric chloride solution to give progressively increasing copper contents. The relative amounts were adjusted so that each catalyst had the same total gram atom metal content as the 0.6% wt. Pt on alumina but varying atomic ratios of Pt and Co, 90:10, 80:20, 70:30 and so on. A catalyst with 100% Cu was also prepared.

Each catalyst was dried at 110° C. overnight, reduced in 4000 v./v./hr. of hydrogen at 500° C. for 3 hours, and

## EXAMPLE 3

Alumina, obtained by calcination of an alumina hydrate precursor in which the trihydrates predominated, having a surface area of 242 m.<sup>2</sup>/g., a pore volume of 0.37 ml./g., and a particle size of 60 to 80 BSS mesh was impregnated with sufficient chloroplatinic acid to give a catalyst containing 0.6% wt. platinum. A series of platinum and cobalt catalysts was also prepared by progressively reducing the concentration of chlor-platinic acid in the solution and impregnating the Pt-Al<sub>2</sub>O<sub>3</sub> with solutions of cobalt chloride of progressively increasing concentration. The relative amounts were adjusted so that each catalyst had the same total gram atom metal content as the 0.6% wt. Pt on alumina but varying atomic ratios of Pt and Co 90:10, 80:20, 70:30 and so on. A catalyst with 100% Co was also prepared.

Each catalyst was dried at 110° C. overnight, reduced in 4000 v./v./hr. of hydrogen at 500° C. for 3 hours, and tested for dehydrocyclisation activity using n-hexane as feedstock and process conditions of 500° C., atmospheric pressure, and 4000 v./v./hr. of feedstock having a 10:1 H<sub>2</sub>:n-hexane mole ratio.

The results obtained are shown in Table 3 below, expressed as conversion rates in millimoles, min.<sup>-1</sup>, gram<sup>-1</sup>.

The results for benzene formation from the n-hexane feedstock (i.e. dehydrocyclisation activity) obtained in Examples 1, 2, and 3 are expressed graphically in the accompanying FIG. 1. The graph clearly shows the large variations in activities depending on the Pt-Cu and Pt-Co atomic ratios and the pronounced peaks corresponding to ordered structures. Those ordered structures with high platinum contents gave significantly higher activities than the catalyst with 100 atomic percent Cu.

The peak at Pt<sub>7</sub>Cu is to be compared with the absence of any peak with Pt-Co, there being no corresponding ordered structure in the Pt-Co system. No measurements were made at 75% Pt 25% Cu or 75% Pt 25% Co (Pt<sub>3</sub>Cu and Pt<sub>3</sub>Co respectively) so the peaks are slightly displaced. Although the Pt-Cu-SiO<sub>2</sub> catalysts were of low activity, the

presence of peaks can still be seen. The catalysts containing 40 atomic percent or less of platinum had relatively low activities but the curves still show a non-linear effect in this region, including a definite peak in the Pt-Co curve.

## EXAMPLE 4

A series of platinum-nickel-alumina and platinum-iron-alumina catalysts were prepared using the same technique as in Example 3 but using nickel chloride ( $\text{NiCl}_2$ ) or iron chloride ( $\text{FeCl}_3$ ) in place of cobalt chloride. The catalysts were tested for dehydrocyclisation activity again using the feedstock and process conditions of Example 3. The results are shown in Tables 4 and 5 below.

TABLE 4.—PLATINUM-NICKEL-ALUMINA

Atomic percent Pt	Rate of formation, millimoles min. <sup>-1</sup> gram <sup>-1</sup>				Selectivity			
	Total conversion	Benzene	Toluene	Xylenes	Benzene	Toluene	Xylenes	Total aromatics
100	0.28	0.13	0.015	0.018	—	—	—	—
90	0.28	0.14	0.004	0.003	50	1.4	1.1	52.5
80	0.29	0.105	0.004	0.004	36.2	1.4	1.4	39
70	0.23	0.123	0.006	0.011	53.5	2.6	4.8	61
60	0.23	0.128	0.007	0.009	55	3.0	3.9	62
50	0.29	0.200	0.017	0.013	69	5.9	4.5	79.5
40	0.25	0.108	0.019	0.009	43	7.6	3.6	54.3
30	0.23	0.108	0.015	0.007	26.8	5.2	2.4	34.2
20	0.23	0.052	0.017	0.011	22.6	7.4	4.8	34.8
10	0.21	0.027	0.012	0.010	12.6	0.6	0.5	13.7
0	0.18	.003	.001	.003	1.7	0.6	1.7	4.0

TABLE 5.—PLATINUM-IRON-ALUMINA

Percent Pt	Rate of formation, millimoles min. <sup>-1</sup> gram <sup>-1</sup>				Selectivity			
	Total conversion	Benzene formation	Xylenes	Toluene	Benzene	Xylenes	Toluene	Total aromatics
100	0.25	0.11	0.018	0.019	44	7.2	7.3	58.5
90	0.20	0.16	0.009	0.006	80	4.5	3.0	88
80	0.23	0.19	0.009	0.009	83	4	4	91
70	0.24	0.15	0.004	0.009	62.5	2	4	68
60	0.25	0.095	0.009	0.009	33	3.5	3.5	55
50	0.20	0.175	0.011	0.004	87.5	5.5	—	95
40	0.21	0.095	0.009	0.009	45	4	4	54
30	0.22	0.12	0.009	0.009	55	4	4	63
20	0.11	0.045	0.03	0.013	42	27	12	81
10	0.18	0.041	0.02	0.013	23	11	7	41
0	—	—	—	—	—	—	—	—

The results for benzene formation obtained in Example 4 are expressed graphically in the accompanying FIG. 2. Also included in FIG. 2 are results with a series of platinum-alumina catalysts of decreasing platinum content. As with FIG. 1 peaks corresponding to ordered structures can be clearly seen, these peaks showing in most instances, a higher activity than a catalyst of 100 atomic percent platinum. The straight-line graph for the Pt- $\text{Al}_2\text{O}_3$  catalysts of decreasing platinum contents provides a base line for comparison and shows that the peaks are not due to any platinum dilution effect.

## EXAMPLE 5

A series of platinum-palladium-alumina catalysts and a series of platinum-tin-alumina catalysts (over the range 100–50 atomic percent Pt) were prepared by the same technique as in Example 3 but using  $\text{PdCl}_2$  and  $\text{SnCl}_2$  in place of cobalt chloride. The catalysts were tested for dehydrocyclisation activity again using the feedstock and process conditions of Example 3. The results for the Pt-Pd- $\text{Al}_2\text{O}_3$  catalysts are shown in Table 6 below.

TABLE 6.—PLATINUM-PALLADIUM-ALUMINA

Percent Pt	Rate of formation, millimole min. <sup>-1</sup> gram <sup>-1</sup>				Selectivity			
	Total conversion	Benzene	Xylenes	Toluene	Benzene	Xylenes	Toluene	Total aromatics
90	0.26	0.16	.006	.007	61.5	2.3	2.7	66.5
80	0.27	0.14	.004	.004	52.5	1.5	1.5	55.5
70	0.27	0.11	.001	.003	41	0.3	1.0	42.3
60	0.22	0.088	Trace	.001	40	—	0.3	40.3
50	0.26	0.12	Trace	.004	46.5	—	1.5	48
40	0.26	0.11	Trace	.004	42.5	—	1.5	44
30	0.20	0.092	.009	.004	46	4.5	2.0	52.5
20	0.19	0.080	Trace	.003	42	—	1.6	43.6
10	0.08	.038	.011	Trace	42	1.3	—	43.3
0	0.07	.014	Trace	Trace	20	—	—	20

The platinum-tin-alumina catalysts showed the following results for rate of benzene formation

Percent Pt:	Rate of benzene formation millimoles min. <sup>-1</sup> gram <sup>-1</sup>
100	0.13
90	0.296
80	0.219
70	0.267
60	0.175
50	0.204

Again with these catalysts, variations throughout the range are seen. The platinum-palladium-alumina catalysts

of Table 6 show maxima at 90 Pt:10Pd (corresponding to the probable ordered alloy structure  $\text{Pt}_7\text{Pd}$ ) and 50 Pt:50 Pd (corresponding to the probable ordered alloy structure  $\text{PtPd}$ ).

The platinum-tin-alumina results are particularly interesting not only in the peaks at 90:10 ( $\text{Pt}_7\text{Sn}$ ) 70:30 ( $\text{Pt}_3\text{Snx}$ ) and 50:50 ( $\text{PtSn}$ ) but also in the marked increase of activity conferred by the tin as compared with the 100% Pt catalyst.

Comparing the best result with each metal in the Examples 2–5 with 100 atomic percent Pt the relative improvement by the incorporation of a second metal in a proportion equivalent to an ordered alloy structure is

100 atomic percent Pt	100
70% Pt 30% Cu ( $\text{Pt}_3\text{Cu}$ )	155
80% Pt 20% Co ( $\text{Pt}_3\text{Co}$ )	140
50% Pt 50% Ni ( $\text{PtNi}$ )	155
80% Pt 20% Fe ( $\text{Pt}_3\text{Fe}$ )	145
90% Pt 10% Pd ( $\text{Pt}_7\text{Pd}$ )	125
90% Pt 10% Sn ( $\text{Pt}_7\text{Sn}$ )	225

## EXAMPLE 6

Samples of the platinum-copper-alumina catalysts of Example 2 having the atomic proportions 70:30, 60:40, and 50:50 were tested for an extended period at elevated pressure under the following conditions

Temperature ----- ° C. 500  
 Pressure ----- p.s.i.g. 350  
 Feedstock ----- n-Heptane  
 Space velocity ----- v./v./hr. 6.0  
 Hydrogen:hydrocarbon mole ratio ----- 7:1  
 Duration ----- hours 48

The products were analysed by gas liquid chromatography and the conversion of the n-heptane to aromatics was as follows:

	Conversion to aromatics, mol percent	
	Initial	Final
70% Pt, 30% Cu.....	50	40
60% Pt, 40% Cu.....	30	20
50% Pt, 50% Cu.....	45	35

These results confirm the previous findings that catalysts with metal contents corresponding to ordered alloy structures (70% Pt 30% Cu  $\approx$  Pt<sub>3</sub>Cu and 50% Pt 50% Cu  $\approx$  PtCu) are significantly more active than a catalyst of 60% Pt 40% Cu corresponding to no ordered alloy structure. The results confirm that this finding applies at elevated pressure and that it is maintained for extended periods.

We claim:

1. A process for the catalytic conversion of hydrocarbons comprising contacting the hydrocarbons at a temperature of 0 to 600° C., a pressure of 0 to 3000 p.s.i.g., a space velocity of 0.1 to 20 v./v./hr. and a hydrogen:hydrocarbon mole ratio of 0 to 20:1 with a catalyst comprising from 0.01 to 10% wt. of metal on a refractory support, said catalyst containing platinum and a second metal which forms a solid solution with platinum, said second metal being selected from the group consisting of cobalt, nickel, iron, copper, tin, palladium, iridium, rhodium, silver, gold, bismuth, mercury, antimony, lead and

cadmium, the atomic amount of platinum in said solid solution being at least 45 atomic percent and being also within  $\pm 5$  atomic percent of the atomic amount of platinum required to form an ordered alloy structure with said second metal, and the atomic amount of said second metal in said solid solution being within  $\pm 5$  atomic percent of the atomic amount of said second metal required to form said ordered alloy structure with the platinum.

2. A process as claimed in claim 1 which is the dehydrogenation or dehydrocyclisation of hydrocarbons having from 3 to 25 carbon atoms at a temperature of 300 to 600° C. a pressure of 0 to 1000 p.s.i.g., a space velocity of 0.1 to 10 v./v./hr. and a hydrogen: hydrocarbon mole ratio of 0 to 20:1.

3. A process as claimed in claim 2 which is the catalytic reforming of a petroleum fraction boiling in the range 15 to 204° C.

4. A process as claimed in claim 1 wherein the second metal is selected from the group consisting of cobalt, nickel, iron, copper, tin and palladium and wherein the platinum and the selected second metal are in atomic amounts which form any one of the following ordered alloy structures: Pt<sub>3</sub>Co, PtCo; PtNi; Pt<sub>3</sub>Fe, PtFe; Pt<sub>7</sub>Cu, Pt<sub>3</sub>Cu, PtCu; Pt<sub>7</sub>Sn, Pt<sub>3</sub>Sn, PtSn; Pt<sub>7</sub>Pd, PtPd.

5. A process as claimed in claim 1 wherein the support is alumina.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—143; 252—466 B, 466 PT; 260—673.5

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,759,823 Dated September 18, 1973

Inventor(s) Evan Ellis Davies, John Stanley Elkins, Robert Chalmers Pitkethly

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 48, change "bu" to - - but - -.

Column 5, line 64, change "0.6" to - - 0.6% - -.

Column 5, line 72, change "Co" to - - Cu - -

Column 7, Table 5, second column from right, under "3.5"

insert - - 2 - -

Signed and sealed this 12th day of March 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents