Patented Feb. 19, 1952

2,586,535

UNITED STATES PATENT OFFICE

2,586,535

CATALYTIC HYDROGENATION OF AROMATIC HYDROCARBONS IN A STAINLESS STEEL REACTOR

Vladimir N. Ipatieff and Herman Pines, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application December 29, 1948, Serial No. 68,093

7 Claims. (Cl. 260—667)

1

This invention relates to a process for hydrogenating aromatic hydrocarbons.

An object of this invention is to convert an aromatic hydrocarbon into a saturated cyclic hydrocarbon.

A further object of this invention is to convert a benzene hydrocarbon into a cycloparaffinic hydrocarbon.

One specific embodiment of this invention relates to a process which comprises hydrogenating an aromatic hydrocarbon in the presence of stainless steel and of a composite comprising copper and alumina.

A further embodiment of this invention relates to a process which comprises hydrogenating a benzene hydrocarbon in the presence of stainless steel and of a composite comprising copper and alumina.

Aromatic hydrocarbons which are employed as starting materials in this process include monocyclic and polycyclic aromatic hydrocarbons. The monocyclic aromatic hydrocarbons comprise benzene, toluene, xylene, mesitylene, ethylbenzenes, propylbenzenes, butylbenzenes, and other alkylbenzenes, containing alkyl groups having more than four carbon atoms, and also benzene hydrocarbons containing a plurality of the same or different alkyl groups. Other aromatic hydrocarbons utilizable in this process include diphenyl, alkylated diphenyl hydrocarbons, naphthalene, alkyl naphthalenes, anthracene, phenanthrene and other hydrocarbons containing a plurality of benzene rings and fused aromatic rings.

We have found that various stainless steels containing nickel have a promoting effect on copper-containing catalysts so that it is possible to convert aromatic hydrocarbons into saturated cyclic hydrocarbons. These stainless steels generally contain from about 10 to 67% of nickel together with smaller percentages of carbon, manganese, silicon, etc. Stainless steels containing both chromium and nickel are also useful in this process for promoting the hydrogenating activity of copper-alumina, copper-zinc-alumina, and other catalysts containing copper and alumina.

The catalysts used in this process include particularly composites containing copper and also alumina, copper-alumina-zinc, and other catalytic materials of relatively low hydrogenating activities that do not promote hydrogenation of the aromatic nucleus of an aromatic hydrocarbon at a temperature below about 200° C. in the presence of stainless steel containing nickel. These catalysts when employed together with stainless steel, the latter used either as the material of

2

the reaction vessel, or in the form of finely divided metal, such as turnings, shavings, etc., have the advantage over the more active catalysts containing relatively large amounts of nickel which promote hydrogenation but at the same time cause a breakage or rupture of the ring of the hydrocarbon undergoing hydrogenation.

A composite of copper and alumina utilizable in the hydrogenation of aromatic hydrocarbons in accordance with the present invention, may be made by the general procedure of coprecipitating basic copper carbonate and aluminum hydroxide. The precipitation may be carried out either at room temperature or at a higher temperature utilizing as the precipitating agent ammonium carbonate, ammonia, or in some cases, a carbonate or hydroxide of potassium or sodium. The precipitated material is then filtered, washed with water to remove soluble salts, dried, formed into particles and then reduced with hydrogen or a gas containing hydrogen prior to use for hydrogenating aromatic hydrocarbons.

The catalysts may also be prepared by carrying out the precipitation at room temperature, followed by heating to approximately 80 or 90° C. or each component may be precipitated first, the other solution added to the reaction mixture and the second component then precipitated upon the first precipitated material. The resulting precipitated mixture is then dried, formed into particles, and reduced as hereinabove described.

Another catalyst comprising essentially copper, zinc, and alumina, and utilizable in this hydrogenation process may be made by the general procedure of precipitating the carbonates of zinc and copper from aqueous solutions of the metallic salts, particularly the nitrates, by the addition of soluble carbonates, particularly ammonium carbonate, in amounts slightly in excess of those required for complete precipitation. The precipitation may be made at ordinary temperatures or at a temperature up to approximately 100° C. The total suspended material including precipitates of zinc carbonate and copper carbonate on alumina is then filtered, washed carefully with water to remove soluble salts, dried at temperature of from approximately 180° to 200° C. for from about 10 to about 20 hours and then pelleted or otherwise formed into particles of different size and shape, usually with the addition of a small amount of a pelleting lubricant such as, for example, a hydrogenated vegetable or animal oil. The resultant particles are then subjected to the action of dry hydrogen at tem-

perature up to about 600° C. which results in the removal of a substantial portion of the lubricating material and in the reduction of the carbonates, first to the oxides and then to the metals. Also the pellets may be dried first with dry air or other gases to remove the lubricant before reduction. The composited catalyst containing copper, zinc, and alumina is also prepared by co-precipitating copper carbonate, zinc carbonate, and alumina or the precipitation procedure may be varied so that zinc carbonate is precipitated first on alumina followed by precipitation of the basic copper carbonate on the mixture. The resulting precipitated materials are dried, pelleted, and reduced as hereinabove set forth.

The proportions of zinc, copper and alumina in the composites prepared and reduced by the above general methods, are varied carefully to produce catalysts of different activities. Good catalysts are prepared, for example, consisting of 25 parts by weight of zinc, 25 parts by weight of copper, and 50 parts by weight of alumina, while others consist of approximately equal parts by weight of zinc, copper, and alumina. Catalysts still exhibit high activity when the zinc concentration is approximately 7% and the copper concentration is approximately 3.5% by weight.

Particles of copper-alumina and copper-zinc-alumina catalysts prepared as indicated frequently contain incompletely reduced copper oxide, or zinc oxide and copper oxide. These catalysts are utilizable as fillers, in suitable heated reactors through which the unsaturated cyclic hydrocarbon to be hydrogenated and hydrogen are passed in the presence of stainless steel and in the presence or absence of a suitable hydrocarbon solvent and at a temperature of from about 200° to about 400° C. The catalyst temperature, hydrocarbon charging rate, and ratio of hydrogen to hydrocarbon are chosen to give the optimum degree of conversion to saturated cyclic hydrocarbons as desired, with a relatively low rate of accompanying decomposition. Also hydrogenation of an aromatic hydrocarbon is effected in the presence of stainless steel and of powdered catalyst mixed with the hydrocarbon and passed through a suitable reactor operated at substantially the temperature and pressure conditions indicated. The reaction products formed in the presence of either a fixed catalyst or powdered catalyst are separated from the catalytic material and fractionated to separate desired products from unconverted charging material and decomposition products. Said unconverted charging material is recycled to further contact with the hydrogenating catalyst to form an additional quantity of desired hydrogenation product.

Batch-type hydrogenation of an aromatic hydrocarbon may be carried out by subjecting said hydrocarbon and catalyst in the presence of stainless steel in an autoclave at a temperature of from about 200° to about 400° C. and a pressure of from about 50 to about 200 atmospheres.

After the hydrogenation reaction has proceeded for a time sufficient to convert a substantial proportion of the aromatic hydrocarbon into saturated cyclic hydrocarbon, the hydrogenation products are separated from the catalyst. Fractional distillation or other suitable means is then employed to separate the desired hydrogenation products from unconverted and incompletely converted starting material and to return such aromatic compounds to further hydrogenation treatment.

The following examples indicate results obtained in the operation of this process, although the data are given with no intention of limiting the generally broad scope of the invention.

p-Cymene was subjected to treatment with hydrogen in the presence of copper-alumina catalyst prepared by reducing a composite of 67% CuO and 33% Al_2O_3.

The hydrogenation treatment was carried out in rotating autoclaves constructed of steel and stainless steel and having a capacity of 450 cc. each. In each run 60 grams of p-cymene and 6 grams of copper-alumina composite (67% CuO–33% Al_2O_3) were heated at a temperature of 325° C. for 6 hours in the presence of hydrogen charged to the autoclave at an initial pressure of 100 atmospheres (measured at 25° C.). The experimental results which are submitted in the table show that in an ordinary steel autoclave, no reaction occurred in the absence of added catalysts (Experiment 1). At the same conditions, but in the presence of copper-alumina catalyst (Experiment 2) only 2% of the p-cymene was hydrogenated and no hydrogenolysis to lower boiling aromatic hydrocarbons occurred. When a similar experiment was made in a stainless steel autoclave but in the absence of copper-alumina (Experiment 3) also no reaction occurred. However, in Experiment 4, carried out in steel autoclave and in the presence of copper-alumina catalysts, 48% of the p-cymene was hydrogenated to p-menthane and about 2% of the p-cymene underwent hydrogenolysis to form lower boiling aromatic hydrocarbons.

Similar effect of the promoting action of stainless steel upon copper-alumina catalysts was observed in another run in which the reaction mixture of p-cymene and copper-alumina catalyst was placed in a stainless steel liner inserted in the autoclave constructed from ordinary steel.

Table.—The effect of stainless and ordinary steel autoclave upon the degree of hydrogenation of p-cymene

Experiment	1	2	3	4
Autoclave [1]	Steel	Steel	[3]	[3]
Catalyst	None	$CuO–Al_2O_3$	None	$CuO–Al_2O_3$
Weight percent of: [2]				
p-Cymene	100	98	100	42.
p-Menthane	0	2	0	48.
Lower Boiling Aromatics				10.

[1] The following is the composition of the steel as recorded by the manufacturer: The ordinary steel autoclave was made of a steel which contained: Carbon, 0.15–0.25%; Manganese, 0.30–0.60%; Phosphorus, 0.045% max.; Sulphur, 0.50% min. The stainless steel autoclave was made of a type of 18–8 steel which contained: Carbon, 0.08%, Manganese, 2.00%; Silicon, 0.5% max.; Chromium, 18–20%; Nickel, 8–10%.

[2] Determined by ultraviolet absorption analysis using the band at 273.5 mμ for calculation purposes.

[3] Stainless steel.

We claim as our invention:

1. A process which comprises hydrogenating an aromatic hydrocarbon in the presence of nickel-containing stainless steel and of a catalyst composite comprising copper and alumina.

2. A process which comprises hydrogenating a benzene hydrocarbon in the presence of nickel-containing stainless steel and of a catalyst composite comprising copper and alumina.

3. A process which comprises hydrogenating an aromatic hydrocarbon at a temperature of from about 200° to about 400° C. in the presence of nickel-containing stainless steel and of a catalyst composite comprising copper and alumina.

4. A process which comprises hydrogenating

an aromatic hydrocarbon at a temperature of from about 200° to about 400° C. in the presence of stainless steel containing nickel and chromium and of a catalyst composite comprising copper and alumina.

5. A process which comprises hydrogenating a benzene hydrocarbon at a temperature of from about 200° to about 400° C. at a pressure of from about 50 to about 200 atmospheres and in the presence of stainless steel containing nickel and chromium and of a catalyst composite comprising copper and alumina.

6. A process which comprises hydrogenating an aromatic hydrocarbon at a temperature of from about 200° to about 400° C. at a pressure of from about 50 to about 200 atmospheres and in the presence of nickel-containing stainless steel and of a catalyst comprising essentially the material formed by subjecting to reduction a composite of copper oxide, zinc oxide, and alumina.

7. A process which comprises hydrogenating a benzene hydrocarbon at a temperature of from about 200° to about 400° C. at a pressure of from about 50 to about 200 atmospheres, and in the

presence of nickel-containing stainless steel and of a catalyst comprising essentially the material formed by subjecting to reduction a composite of copper oxide, zinc oxide, and alumina.

VLADIMIR N. IPATIEFF.
HERMAN PINES.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,236,853	McKee	Aug. 14, 1917
1,255,590	Ellis	Feb. 5, 1918
2,109,119	Naumann	Feb. 22, 1938
2,355,219	Ipatieff et al.	Aug. 8, 1944
2,430,416	Weizmann	Nov. 4, 1947

OTHER REFERENCES

"Conversion of Petroleum," by A. N. Sachanen, Reinhold Publishing Corp., New York, 1940, pages 86–89; 196–198.