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PROCESS FOR HYDROGENATING AROMATIC HYDROCARBONS

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This application is a continuation in part of applicants' copending application having the same title, Serial No. 811,556, filed May 7, 1959, now abandoned.

This invention relates to a hydrogenating process and more particularly to a process for catalytically hydrogenating aromatic hydrocarbons.

Processes have been suggested in the prior art for hydrogenating aromatic hydrocarbons. However, these processes have certain disadvantages with respect to ultimate yields obtained or to commercial feasibility. Generally such processes are batch procedures and in some cases are liquid phase operations or require relatively high temperatures of reaction. Where the process is liquid phase, relatively high pressures are required with the resulting need for comparatively costly high pressure equipment. Where such prior art processes require relatively high temperatures there is a correspondingly high requirement of heat energy and accordingly the exit product vapors require a greater amount of cooling.

It is an object of this invention to provide a continuous, vapor-phase process for hydrogenating aromatic hydrocarbons.

Another object of this invention is to provide a commercially feasible process for hydrogenating aromatic hydrocarbons to hydrogenated products of high purity.

A further object of this invention is to provide a truly continuous process for hydrogenating aromatic hydrocarbons under conditions such that the desired hydrogenated products may be readily and cheaply prepared.

Another object of the invention is to provide a vapor-phase process for hydrogenating aromatic hydrocarbons at relatively low temperatures and with substantially quantitative conversions.

A further object of the invention is to provide a catalytic process for producing completely hydrogenated products from aromatic hydrocarbons wherein a given weight of catalyst used may be employed continuously without regeneration over a longer period of time than heretofore known.

In accordance with the invention these objects are accomplished by a process in which the aromatic hydrocarbon is contacted in the vapor phase in the presence of the specially-reduced nickel catalyst under hydrogenation conditions, i.e., in the presence of hydrogen at moderately elevated temperatures below about 300° C., preferably not in excess of about 225° C., e.g., an average temperature in the range of about 60–120° C.

The aromatic hydrocarbons hydrogenated according to this invention include benzene and benzene derivatives, for example, Tetralin (1,2,3,4-tetrahydronaphthalene); naphthalene; alkyl-substituted benzenes in which the total substituent portion has from one to six carbon atoms, e.g., toluene, n-butylbenzene, o-, m-, and p-xylene, mesitylene, etc.; and the like.

The specially-reduced catalyst employed in the process of this invention is a nickel catalyst, e.g., nickel hydrate, which has been reduced at a temperature below about 450° C., reoxidized by passing a gas containing free oxygen over the reduced catalyst, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

Subsequent to reducing the nickel catalyst at a temperature below about 450° C., as described above, the nickel catalyst material is preferably partially reoxidized by passing a gas containing free oxygen thereover until the ratio of reduced nickel to total nickel is about 55%. The final reduction of the novel material is then preferably obtained by passing a gas thereover initially containing about 5% hydrogen and about 95% nitrogen, the hydrogen content having been progressively increased to 100% so that the temperature of the latter reduction step is maintained below about 250° C.

The specially-reduced nickel catalyst may be used as such or it may be supported on any suitable support such as kieselguhr, alumina, pumice, alundum, charcoal or the various natural or synthetic clay-like supports that are well known to the art. In addition, the catalyst composition may be modified if desired to incorporate certain basic substances such as sodium silicate, calcium oxide, magnesium oxide or the like.

The hydrogenating temperature employed depends, in part, on the particular aromatic hydrocarbon to be hydrogenated. For example, average catalyst temperatures may be in the range of about 95° C. to about 120° C. when the aromatic hydrocarbon to be hydrogenated is Tetralin; about 65° C. to about 100° C. in the case of benzene; about 60° C. to about 95° C. in the case of toluene; and about 60° C. to about 85° C. in the case of ethylbenzene.

While it is a characteristic of the process of this invention that substantially 100% conversion can be obtained at such relatively-low average hydrogenating temperatures, e.g., about 60° C. to about 120° C., in practice the exothermic nature of the reaction usually results in the formation of a hot zone in the catalyst bed at and/or adjacent to the reaction front, the temperature of which may be substantially above the minimum and preferred temperature for obtaining substantially 100% conversion. The maximum temperature of such hot zones should be controlled so as to avoid undesired side reactions, e.g., back dehydrogenation of the product and/or excessive cracking, i.e., hydrogenolysis of the rings and/or substituents to form normally-gaseous products.

For example, when hydrogenating Tetralin substantially 100% conversion can be obtained at hydrogenating temperatures from below about 100° C. up to about 160° C. Should the maximum temperature of the hot zone in the catalyst bed exceed about 160° C., however, back dehydrogenation begins to occur and yield of Decalin (decahydronaphthalene) begins to decline, e.g., to as low as 45% at a maximum hot-zone temperature of 210° C. If the maximum hot-zone temperature is allowed to increase still further, substantial ring hydrogenolysis to normally-gaseous products occurs at about 225° C. and above.

These and other data on a wide variety of aromatic hydrocarbons indicate, in general, that ring hydrogenolysis occurs at about 225° C. and that substituents are subject to hydrogenolysis at about 170° C. They also indicate that the amount of hydrogenolysis of a substituent and the temperature at which hydrogenolysis occurs depends, in part, on the size, type, and position of the substituent. For example, the methyl groups of 1,2-dimethylbenzene are more readily subject to hydrogenolysis than are the methyl groups of 1,3,5-trimethylbenzene. Also, ethyl or higher alkyl groups are subject to hydrogenolysis at even lower temperatures, but the number of carbon atoms above two do not appear to have any substantial effect on hydrogenolysis temperature.

To avoid such product loss, the maximum hot-zone temperature should, therefore, be controlled so as not to exceed the temperature at which such undesired side reactions, e.g., back dehydrogenation and/or cracking, oc-

cur to an excessive degree. The temperature for any particular hydrocarbon is readily determinable by those skilled in the art in the light of the above disclosure and specific embodiments hereinafter set forth. For example, the maximum hot-zone temperature in the case of Tetralin or naphthalene should not substantially exceed about 170° C.; for benzene, about 225° C.; for toluene, about 210° C.; for ethylbenzene, about 170° C.; for n-butylbenzene, about 170° C.; for xylenes, about 170° C.; and for mesitylene, about 180° C.

The above generalizations with respect to hydrogenating temperature are based on experimental data obtained by means of a sliding thermocouple in the center of an elongated cylindrical catalyst bed of a pilot plant reactor having an internal diameter of about 1.4 inches. The temperatures stated are based on observations of the highest temperatures encountered as the thermocouple is moved axially through the catalyst bed. While the temperatures are the highest temperatures read, it should be understood that they are not necessarily the highest temperatures at the individual catalytic sites of each catalyst pellet. Limitations of standard pilot-plant temperature-measuring equipment prevent further definitive information in this regard. The integrated average temperature of the entire catalyst bed is, of course, substantially less than the maximum permissible hot-zone temperatures indicated above.

The pressure that is employed in the reaction is preferably not substantially in excess of atmospheric pressure and ordinarily the pressures that are used in the process are only those that are incident to moving the vaporous reactants through the catalyst bed. Thus by the term "not substantially in excess of atmospheric" pressure is meant to include those higher pressures which may in certain cases be as high as two or three atmospheres, it being recognized that the process of this invention is essentially a low pressure operation and that moderately higher pressures could be employed incident to moving the reaction products through the reaction column without departing from the spirit and scope of this invention. It should also be understood that the process is operative at still higher pressures; and if other considerations dictate a substantially higher pressure than that required to move reactants, such higher pressure may also be employed without departing from the spirit and scope of this invention.

The invention is further illustrated but is not limited by the following examples in which feed and product analyses were obtained by vapor phase chromatography. Quantities stated are in parts by weight unless otherwise indicated.

Example 1

A specially-reduced and stabilized nickel catalyst was prepared by the following procedure. Unreduced nickel kieselguhr tablets were loaded into a vertical reactor. The system was purged with nitrogen and brought to about 260° C. Hydrogen flow was started and the temperature gradually increased to about 427° C. This temperature was maintained by circulating the hydrogen through an external heater. It was necessary to dry the circulating gases by passing them through an external dryer. When the formation of water had virtually stopped, the system was cooled to about 32° C. while maintaining hydrogen flow. When the system had reached this temperature it was purged with nitrogen. The reduced catalyst was partially reoxidized by adding a small quantity of oxygen with the inert gas. The temperature was maintained below about 57° C. by adjusting the amount of oxygen present. The peak temperature was measured and when that temperature reached the bottom of the reactor the stabilization was complete. After stabilization the system was flushed with air to atmospheric conditions. In this form the catalyst contained about 60% nickel with a ratio of reduced nickel to total nickel of about 55%.

The reduced and stabilized catalyst was charged into a column heated by means of a circulating oil in a jacket surrounding the column. The catalyst was reduced by passing pure hydrogen down through the column starting at about 140° C. Over a period of four hours the temperature was gradually raised to about 200° C. and held until no further water was given off. After reduction of the catalyst the temperature was lowered to less than 120° C. Tetralin was then vaporized into a stream of pre-heated hydrogen by introducing the Tetralin into a heated vaporizing chamber through which the pre-heated hydrogen was passed. The resulting mixture was then passed through the catalyst column as a vapor. The operating pressure was about one to two pounds per square inch gauge which was just enough to cycle the vapor through the system. The vapor stream emerging from the catalyst column was passed through a condenser into a chilled container to condense the reaction product.

The foregoing process was carried out under conditions wherein the Tetralin was fed at a rate of 0.107 part per hour per part catalyst, the hydrogen flow was 26 moles per hour per mole of Tetralin fed, and the temperature of the reaction column was maintained at about 100° C., as indicated by the temperature of the circulating oil in the surrounding jacket, which circulating oil temperature is a rough approximation of the integrated average temperature of the catalyst bed. The conversion of Tetralin was 100%. The product analyzed 100% by weight Decalin (25% cis and 75% trans).

Example 2

The procedure of Example 1 was repeated with the following exceptions. The aromatic hydrocarbon hydrogenated was benzene and the feed rate was 0.143 part per hour per part. The hydrogen flow was 12 moles per hour per mole of feed. The temperature of the reaction column as indicated by the circulating oil temperature was maintained at about 80° C. The conversion of benzene was 100%. The product analyzed 99.6% by weight cyclohexane.

Example 3

The procedure of Example 2 was repeated with the following exceptions. The feed rate was 0.08 parts per hour per part catalyst. The hydrogen flow was 30 moles per hour per mole of feed. The temperature of the reaction column as indicated by the circulating oil temperature was maintained at about 95° C. The conversion of benzene was 100%. The product analyzed 99.8% by weight cyclohexane. The process was run continuously for 2400 hours with no indication of deactivation of the catalyst.

Example 4

The procedure of Example 1 was repeated with the following exceptions. The aromatic hydrocarbon hydrogenated was toluene and the feed rate was 0.164 part per hour per part catalyst. The hydrogen flow was 20 moles per hour per mole of feed. The temperature of the reaction column as indicated by the circulating oil temperature was maintained at about 85° C. The conversion of toluene was 100%. The product analyzed 100% by weight methylcyclohexane.

Example 5

The procedure of Example 4 was repeated with the following exceptions. The feed rate of toluene was 0.104 part per hour per part catalyst. The hydrogen flow was 25 moles per hour per mole of feed. The temperature of the reaction column as indicated by the circulating oil temperature was maintained at about 90° C. The conversion of toluene was 100%. The product analyzed 100% by weight methylcyclohexane. The process was run continuously for 960 hours with no indication of deactivation of the catalyst.

Example 6

The procedure of Example 1 was repeated with the following exceptions. The aromatic hydrocarbon hydrogenated was ethylbenzene at a feed rate of 0.100 part per hour per part catalyst. The hydrogen flow was 25 moles per hour per mole of feed. The temperature of the reaction column as indicated by the circulating oil temperature was maintained at about 80° C. The conversion of ethylbenzene was 100%. The product analyzed 93% by weight ethylcyclohexane.

Example 7

The procedure of Example 1, including the use of a nickel catalyst prepared in the same manner, was substantially repeated with the following exceptions. The aromatic hydrocarbon was benzene, and the feed rate was about 0.7 part per hour per part catalyst. The hydrogen flow was about 15 mole per hour per mole of feed. The temperature of the hot zones in the catalyst bed was maintained in the range of about 200–240° C., although the average temperature of the entire catalyst bed was maintained at about 70° C., as indicated by the circulating oil temperature. The conversion of benzene to cyclohexane is indicated by the following inspections of the drums of feed stock and product:

FEED STOCK INSPECTIONS

	Wt. percent	
	1st Drum	2nd Drum
Benzene	99.52	98.85
Low Boilers	0.04	0.05
High Boilers	0.44	1.11

PRODUCT INSPECTIONS

	Wt. percent	
	1st Drum	2nd Drum
Benzene	None	None
Cyclohexane	99.07	98.76
Low Boilers	0.44	0.16
High Boilers	0.43	1.08

The process was run substantially continuously for 580 hours with no indication of catalyst deactivation (i.e., no shift in the hot zone). During this period over 403 pounds of cyclohexane was produced per pound of catalyst.

Example 8

To evaluate the effect of hot-zone temperature as measured by a sliding thermocouple in the center of the catalyst bed, a series of runs were made employing substantially the same procedures and catalyst as outlined in Example 1. Both Tetralin and naphthalene were employed as feed stocks with both giving the same results, as hereinafter set forth. The feed rate in each case was about 0.092 part per hour per part catalyst and the hydrogen flow was 42 moles per hour per mole of feed. The results are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. Percent		
	Decalin	Tetralin	Naphthalene
Up to 160	100	0	0
167	98	2	0
180	92	8	0
200	60	39	1
210	45	52	3

Cracking to gaseous products in significant amounts (1%) was observed at a hot-zone temperature of about 225° C.

Example 9

The procedure of Example 8 was repeated with several exceptions. The aromatic hydrocarbon hydrogenated was ethylbenzene, and the feed rate was about 0.083 part per hour per part catalyst. The hydrogen flow was about 17 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. Percent		
	Ethyl-Cyclohexane	Methyl-Cyclohexane	Cyclohexane
Up to 160	100	0	0
166	98	2	0
173	95	5	0
180	90	10	0
186	80	19	1
189	70	29	1

Ring hydrogenolysis appeared to start at a maximum hot-zone temperature of about 210° C. and became significant at about 225° C.

Example 10

The procedure of Example 8 was repeated with several exceptions. The aromatic hydrocarbon hydrogenated was toluene, and the feed rate was about 0.082 part per hour per part of catalyst. The hydrogen flow was about 15 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. Percent	
	Methyl-Cyclohexane	Other
Up to 210	100	0
213	98	2
218	95	5
225	90	10

Ring hydrogenolysis was definite at a maximum hot-zone temperature of about 225° C.

Example 11

The procedure of Example 8 was repeated with several exceptions. The aromaitc hydrocarbon hydrogenated was benzene, and the feed rate was about 0.073 part per hour per part of catalyst. The hydrogen flow was about 13 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. percent	
	Cyclohexane	Other
Up to 225	100	0
230	98	2
237	95	5
243	90	10
249	80	20
253	70	30

Ring hydrogenolysis to the extent of 2% was observed at a maximum hot-zone temperature of about 230° C.

Example 12

The procedure of Example 8 was repeated with several exceptions. The aromatic hydrocarbon hydrogenated was n-butylbenzene, and the feed rate was about 0.084 part per hour per part of catalyst. The hydrogen flow was

about 45 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. percent	
	n-Butyl-Cyclo-hexane	Other
Up to 160-170	100	0
172	98	2
188	95	5
199	90	10
209	80	20

Example 13

The procedure of Example 8 was repeated with several exceptions. The aromatic hydrocarbon hydrogenated with xylene (a mixture of 1,2-; 1,3-; and 1,4-dimethylbenzene), and the feed rate was about 0.090 part per hour per part of catalyst. The hydrogen flow was about 39 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. percent	
	Dimethyl-Cyclo-hexane	Other
Up to 170	100	0
178	98	2
192	95	5
207	90	10
220	80	20

Example 14

The procedure of Example 8 was repeated with several exceptions. The aromatic hydrocarbon hydrogenated was mesitylene, and the feed rate was about 0.084 part per hour per part of catalyst. The hydrogen flow was about 44 moles per hour per mole of feed. The results obtained are as follows:

Max. Hot-Zone Temp., ° C.	Product Inspection, Wt. percent	
	1,3,5-Tri-methyl-Cyclo-hexane	Other
Up to 170-175	100	0
184	98	2
190	95	5
195	90	10
202	80	20

While particular embodiments of this invention have been described hereinabove, it will be understood. of course, that the invention is not limited thereto. Many modifications will be apparent from the above description to those skilled in the art, and it is contemplated by the claims of this specification to cover any such modifications as fall within the true spirit and scope of this invention.

Having thus described the invention, what is claimed is:

1. A process for hydrogenating an aromatic hydrocarbon selected from the group consisting of Tetralin, naphthalene, benzene, and alkyl-substituted benzenes, the total substituent portion of said alkyl-substituted benzenes having from 1 to 6 carbon atoms, which process comprises contacting said aromatic hydrocarbon in the vapor phase and under hydrogenation conditions with a nickel catalyst which has been reduced at a temperature below about 450° C., reoxidized by passing a gas containing free oxygen over the reduced catalyst, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

2. A process for hydrogenating an aromatic hydrocarbon selected from the group consisting of Tetralin, naphthalene, benzene, and alkyl-substituted benzenes, the total substituent portion of said alkyl-substituted benzenes having from 1 to 6 carbon atoms, which process comprises contacting said aromatic hydrocarbon in the vapor phase with hydrogen at a temperature below about 300° C. in the presence of a nickel catalyst which has been reduced at a temperature below about 450° C., reoxidized by passing a gas containing free oxygen over the reduced catalyst, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

3. The process of claim 2 wherein said catalyst is nickel hydrate which has been reduced at a temperature below about 450° C., partially reoxidized by passing a gas containing free oxygen thereover, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

4. The process of claim 2 wherein said nickel catalyst has been reduced at a temeprature below about 450° C., partially reoxidized by passing a gas containing free oxygen thereover until the ratio of reduced nickel to total nickel is about 55%, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

5. The process of claim 2 wherein said nickel catalyst has been reduced at a temperature below about 450° C., partially reoxidized by passing a gas containing free oxygen thereover until the ratio of reduced nickel to total nickel is about 55%, and again reduced by passing a gas thereover initially containing about 5% hydrogen and about 95% nitrogen, said hydrogen content having been progressively increased to 100%, whereby the temperature of the latter reduction step is maintained below about 250° C.

6. A process for hydrogenating an aromatic hydrocarbon selected from the group consisting of Tetralin, naphthalene, benzene, and alkyl-substituted benzenes, the total substituent portion of said alkyl-substituted benzenes having from 1 to 6 carbon atoms, which process comprises contacting said aromatic hydrocarbon in the vapor phase with hydrogen at a maximum hydrogenating temperature not substantially in excess of about 225° C. in the presence of a nickel catalyst which has been reduced at a temperature below about 450° C., reoxidized by passing a gas containing free oxygen over the reduced catalyst, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

7. The process of claim 6 wherein said aromatic hydrocarbon is Tetralin and said maximum hydrogenating temperature is a temperature not substantially in excess of about 160° C.

8. The process of claim 6 wherein said aromatic hydrocarbon is naphthalene and said maximum hydrogenating temperature is a temperature not substantially in excess of about 160° C.

9. The process of claim 6 wherein said aromatic hydrocarbon is toluene and said hydrogenating temperature is a temperature not substantially in excess of about 210° C.

10. The process of claim 6 wherein said aromatic hydrocarbon is ethylbenzene and said maximum hydrogenating temperature is a temperature not substantially in excess of about 170° C.

11. The process of claim 6 wherein said aromatic hydrocarbon is n-butylbenzene and said maximum hydrogenating temperature is a temperature not substantially in excess of about 170° C.

12. The process of claim 6 wherein said aromatic hydrocarbon is a xylene and said maximum hydrogenating temperature is a temperature not substantially in excess of about 170° C.

13. The process of claim 6 wherein said aromatic hydrocarbon is mesitylene and said hydrogenating tempera-

ture is a temperature not substantially in excess of about 180° C.

14. A process for hydrogenating benzene which comprises contacting benzene in the vapor phase with hydrogen at a maximum hydrogenating temperature not substantially in excess of about 225° C. in the presence of a nickel catalyst which has been reduced at a temperature below about 450° C., reoxidized by passing a gas containing free oxygen over the reduced catalyst, and again reduced by passing a gas thereover containing free hydrogen at a temperature below about 250° C.

References Cited in the file of this patent

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