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ACTIVATION OF METALS FOR HYDROCARBON DEHYDROGENATION

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This invention relates to the dehydrogenation of hydrocarbons to substances having the same number of carbon atoms per molecule such as naphthenes to aromatics, paraffins to olefins, and olefins to diolefins. In a more specific sense, the invention is concerned with activation of massive nickel, iron-nickel alloys and iron-manganese alloys, including stainless steels, to impart dehydrogenation activity thereto and to the catalyst so obtained.

It is often desirable to dehydrogenate various hydrocarbons to produce more unsaturated materials suitable for a variety of purposes. Dehydrogenation reactions commonly employed include dehydrogenation of butenes to butadienes, dehydrogenation of butane to butenes, dehydrogenation of other paraffins to corresponding olefins and dehydrogenation of naphthenes to produce aromatics.

It has heretofore been known to employ as dehydrogenation catalysts, transition metal oxides such as the oxides of chromium, molybdenum and vanadium alone or supported on alumina or other difficulty reducible oxide support or group VIII metals deposited on a high surface area support.

Massive metals and alloys have been used as catalysts in liquid phase hydrogenation reactions. Thus, the success of such bulk metal catalysts as Raney nickel, Adams platinum and palladium black resides in a novel preparation of a skeletal structure. In general, the active forms of massive metal catalysts such as the above cannot withstand the high temperature requirements for dehydrogenation reactions. Thermodynamics permits the attainment of appreciable rates of hydrogenation at room temperature for most unsaturated hydrocarbons while the necessity of temperatures in excess of 700° F. for hydrocarbon dehydrogenation reactions causes rapid sintering of any previously known high area massive metal catalyst. Accordingly, Raney nickel, Adams platinum and palladium black are effective as liquid phase hydrogenation catalysts while very dilute supported platinum is used as a vapor phase dehydrogenation catalyst.

The present invention has as its principal object the provision of an improved massive metal catalyst suitable for the dehydrogenation of hydrocarbons. A further object of the invention is to provide a method for activating metals to afford resulting products characterized by a hydrocarbon dehydrogenation activity. A further object of the invention is to provide an improved process for the dehydrogenation of dehydrogenatable hydrocarbons. Other objects and advantages of the invention will be apparent to those skilled in the art from the description set forth hereinbelow.

In one embodiment, the present invention comprises imparting hydrocarbon dehydrogenation activity to nickel and alloys of nickel or manganese with iron by contacting the same in a finely divided state with an ammonia-steam atmosphere at an elevated temperature within the

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approximate range of 800 to 1300° F. for a period sufficient to improve the hydrocarbon dehydrogenation activity of the product over the untreated metal or alloy and generally for a period in excess of ½ hour.

In another embodiment, the present invention comprises imparting hydrocarbon dehydrogenation activity to nickel, iron-nickel alloys and iron-manganese alloys by contacting the same, in a finely divided state, with ammonia at an elevated temperature within the approximate range of 800 to 1300° F. for a period sufficient to improve the hydrocarbon dehydrogenation activity of the product over the untreated metal or alloy and generally for a period in excess of ½ hour.

In a still further embodiment, the present invention comprises a process for dehydrogenating hydrocarbons by subjecting a dehydrogenatable hydrocarbon to the action of a catalyst at dehydrogenation conditions, said catalyst having been prepared by contacting nickel, iron-nickel alloys or iron-manganese alloys in a finely divided state with ammonia at an elevated temperature within the approximate range of 800 to 1300° F. for a period sufficient to improve the hydrocarbon dehydrogenation activity of the product over the untreated metal or alloy and generally for a period in excess of ½ hour.

In still another embodiment, the present invention comprises a hydrocarbon dehydrogenation catalyst prepared by contacting nickel, iron-nickel alloys or iron-manganese alloys in a finely divided state with ammonia at an elevated temperature within the approximate range of 800 to 1300° F. for a period sufficient to improve the hydrocarbon dehydrogenation activity of the product over the untreated metal or alloy and generally for a period in excess of ½ hour.

The method of activating massive nickel, iron-nickel alloys and iron-manganese alloys in accordance with the present invention comprises contacting the same at an elevated temperature with ammonia during which time the iron in the iron-containing alloys is converted into iron nitride, but no appreciable formation of nickel nitride occurs. A manyfold increase in the hydrocarbon dehydrogenation activity of pure nickel, iron-nickel alloys or iron-manganese alloys is obtained as a result of such activating treatment. No activity, however, is obtained when pure iron or when alloys of aluminum and nickel are treated in this manner.

Without being limited by any theory, it is believed that the catalytic dehydrogenation activity achieved is attributable, in the case of the iron-nickel alloy to nearly complete conversion to iron nitride-nickel which in turn results in an expansion of the iron lattice throughout the alloy. It is believed that the strains involved at the nickel sites when the iron lattice, with which the nickel is in solid solution, is expanded result in a highly active specie of nickel becoming available as dehydrogenation sites. A similar effect is believed to take place in the case of the iron-manganese alloy. In the case of pure nickel, it is believed that the specified high temperature treatment with ammonia serves to create defects in the nickel lattice which in turn gives rise to the observed catalytic activity.

The activated massive nickel, iron-nickel alloy or iron-manganese alloy may be used as a single dehydrogenation catalyst or may be intimately combined or incorporated with other materials of an acidic nature so that the resulting composite possesses both dehydrogenation and cracking activities required for many hydrocarbon conversion processes carried out in the presence of hydrogen such as for example, reforming and hydrocracking operations.

The massive metal-containing charge materials which may be effectively treated in accordance with the method of the invention include pure nickel, alloys of iron and nickel in which the nickel content may be as low as 1 percent by weight. The iron-nickel alloys may contain minor proportions of various other elements including chromium, silicon, molybdenum, vanadium and manganese. Thus, various stainless steels comprising a major proportion of iron together with minor proportions of nickel and chromium may be effectively treated in accordance with the process of the invention to impart hydrocarbon dehydrogenation activity thereto. Alloys of manganese and iron, for example Hadfield metal containing 10 to 14 percent by weight of manganese and remainder iron, may also be effectively treated in accordance with the process of the invention to impart substantial dehydrogenation activity thereto.

Heating of massive nickel, iron-nickel alloys or iron-manganese alloys of the type described above in ammonia at a temperature in the approximate range of 800 to 1300° F. for at least about ½ hour is generally sufficient to properly activate the nickel or iron-containing alloy and to provide catalysts of considerably higher activity for dehydrogenation hydrocarbons than the massive nickel or iron-containing alloy which has not undergone the activation treatment. While activation is facilitated by an increase in temperature, a temperature substantially the same as or slightly above the operating temperature of the dehydrogenation step is preferred since little or no subsequent cooling is thereby required. The pressure of the ammonia is not particularly critical and may be any conventionally employed pressure such as atmospheric or higher. While, as indicated above, a treating period of about ½ hour or longer for contact of the massive metal or alloy with ammonia is usually sufficient for the activation, the period of activation may be shorter in some instances.

The catalyst obtained by the method described herein may be used to advantage in the dehydrogenation of any dehydrogenatable hydrocarbon under conditions of time, temperature and pressure within conventional ranges such as 800 to 1100° F., atmospheric pressures up to about 1000 p.s.i., a feed rate of 0.5 to 5 liquid hourly space velocity and hydrogen flow of 500 to 5000 cubic feet of hydrogen per barrel of reactants. The catalyst may suitably be regenerated whenever it becomes inactive by burning-off the deposited coke in an oxygen-containing atmosphere and when necessary, again subjecting the catalyst to the action of ammonia in accordance with the method of the invention.

The metal charge of nickel, iron-nickel alloys or iron-manganese alloys is generally subjected to the specified treatment with ammonia in particle form and generally in a finely divided state such as, for example, in the form of a powder, wire, foil, lathe turnings, or other finely divided state, generally having a particle size of between about 4 and 400 mesh (Tyler) and preferably between about 100 and about 300 mesh (Tyler).

An important embodiment of the invention is the use of a combined ammonia-steam flow through the bed of finely divided nickel or iron-containing alloy. As will be evident, from the data set forth hereinbelow, increased activation is obtained with wet ammonia treatment as compared to treatment with dry ammonia. Thus, the addition of water to the ammonia stream in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30 has been found to result in an increased activation as compared to treatment with ammonia in the absence of such added water.

The specified ammonia treatment either in the wet or dry state converts the iron in the iron-containing alloys such as iron-nickel alloys and iron-manganese alloys to iron nitride. The latter compound has been determined by X-ray diffraction patterns and by chemical analysis.

In connection with this change in the chemical make-up of the alloy, the lattice dimensions are increased as a result of the specified ammonia treatment. It is known that metallic nitrides are true interstitial compounds and it would appear that strains are set up in the alloy matrix. A decrease in the measured real density of the alloys occurs when nitriding takes place which is an indication of the lattice changes which occur. Another physical change which occurs upon the specified treatment with ammonia is the conversion from a non-magnetic alloy in the case where iron is present as gamma iron to a magnetic alloy when iron nitride has been produced. Nickel forms a solid solution with the gamma iron, since the stable form of nickel is in the face-centered cubic lattice like that of gamma iron. When the iron is converted into an iron-nitride, the nickel no longer remains in solid solution. All of the above factors lend support to the supposition that conversion of solid solution nickel-gamma iron alloys to nickel iron nitride creates an alloy structure in which the nickel due to its strained lattice structure, is characterized by a catalytic activity.

The examples set forth hereinbelow will serve to illustrate the invention without limiting the same. The procedure used in these examples was as follows:

Powdered metals and alloys undergoing treatment and having a particle size of approximately 100/200 mesh were diluted with twice their volume of 100/200 mesh Vycor powder and packed into a ¾" inside diameter Vycor tube. The tube was heated in a furnace to a temperature between 850 and 1250° F., usually at 1200° F. under flowing hydrogen at atmospheric pressure. Ammonia flowing at a controlled rate, usually 1 liter per minute, was passed through the tube and in most instances, water was pumped into the ammonia stream just prior to the tube at a rate of 7.5 cc./hour. The amount of ammonia decomposition which occurred during its passage through the tube was about 50 percent under the usual temperature conditions of 1200° F. but such extent of ammonia decomposition could be varied by changing the ammonia rate or the temperature. Some ammonia treatments were made under pressures of up to 100 p.s.i.g. which also decreased the percentage decomposition of the ammonia. Control of the decomposition rate of the ammonia either by flow control or by pressure control was not found to be particularly critical for the present process. The time of ammonia treatment was varied in the experimental examples from 1 to 7 hours and generally was carried out for about 4 hours. It is contemplated that the time of ammonia treatment may extend from about ½ hour to 10 hours or more.

At the completion of the ammonia treatment, the tube was cooled to room temperature under ammonia flow and then purged with nitrogen. The metal particles were separated from the Vycor magnetically and then tested for catalytic activity in a cyclohexane dehydrogenation test. Such test is conducted at 100 p.s.i.g., utilizing a hydrogen to cyclohexane mole ratio of 6, a liquid hourly space velocity of 30 and a temperature of 900° F. The concentration of benzene in the liquid product is determined from refractive index measurements and any cracking activity of the catalyst for cyclohexane is detected by the weight percent recovery of liquid product from the reactor. In the tables of data shown below in the examples of catalytic activity, the mole percent of benzene in the liquid product and the weight percent liquid recovery taken at cyclohexane on-stream times of ¾ hour and 1½ hours are given. Occasional experiments were made for longer periods of time when any rapid decline in activity appeared at 1¼ hours. In Table I below, the improvement in dehydrogenation activity is shown upon treatment of stainless steel containing approximately 10 percent by weight of nickel, 18 percent by weight of chromium, 2 percent by weight of silicon and remainder iron, in the form of a 100/200 mesh powder.

Table I

Example	NH ₃ rate liter/ min.	H ₂ O rate (cc/hr.)	Temp. (° F.)	Length of treat- ment (hrs.)	Dehydrogenation activity			
					¾ hr.		1¼ hrs.	
					Weight percent aro- matics	Weight percent liq. rec.	Weight percent aro- matics	Weight percent liq. rec.
1.....	None	None	1,200	3	<1	100	—	—
2.....	0.46	7.5	1,200	4	26	83	24	84
3.....	0.67	7.5	1,200	4	27	85	25	83
4.....	0.89	7.5	1,200	4	25	89	24	95
5.....	2.05	7.5	1,200	4	23	82	18	84
6.....	0.89	None	1,200	4	15	96	—	—
7.....	0.75	None	1,100	4	19	92	12	92
8.....	0.64	None	1,000	4	16	96	9	98
9.....	0.63	7.5	1,000	4	12	94	11	96

¹ Under H₂.

It will be seen from the above table that the dehydrogenation activity of the activated stainless steel was greatly improved over that of the untreated stainless steel. It will further be seen that a more active and more stable catalyst was obtained when a small amount of water vapor was present in the ammonia treating stream.

In Table II below are shown similar treatment of pure iron and various other iron-nickel alloys in the form of 100/200 mesh powder with ammonia for 4 hours at 1200° F.

Table II

Example	Alloy, name	Metals alloyed with Fe			Ammonia treatment		Percent N in Metal	Dehydrogenation activity			
		Percent Ni	Percent Cr	Other	Rate l./min.	Cc.H ₂ O/hr.		¾ hour		1¼ hours	
								Weight percent arom.	Weight percent liq. rec.	Weight percent arom.	Weight percent liq. rec.
10.....	Electrolytic iron.....				~0.7	~8	5.2	4	90	2	91
11.....	4600 steel.....	2			None	None		1	90		
12.....	Nickel steel ¹	9		1% Mn.....	1.2	7.5	5.9	30	88	24	91
13.....	302 Stainless steel.....	9	19	2% Si.....	0.7	8.2	4.7	20	97	17	98
14.....	316 Stainless steel.....	10	18	2% Mo.....	1.0	7.5	5.4	44	81	41	87
15.....	304 Stainless steel.....	10	18	2% Si.....	1.0	7.5	5.2	46	85	42	89
16.....	310 Stainless steel.....	20	25	2% Si.....	None	None		<1	100		
17.....	50/50 steel.....	49			0.7	7.5	3.6	27	85	25	83
					0.9	7.5	1.5	11	96	11	93
					1.0	7.5	1.0	19	94	16	97

¹ Coarse lathe turnings.

It will be seen from the above table that in the case of Example 10 in which pure iron was subjected to the specified treatment no activation was obtained even though iron nitride was formed. It is also of interest to note from the foregoing table that in the case of Example 11, a nickel containing steel which had a nickel content of only 2 percent by weight possessed a marked dehydrogenation activity after the ammonia treatment.

20 It would appear that high dilution of nickel in the iron nitride matrix is beneficial from the standpoint of activity per atom of nickel.

25 In Table III below, treatment of an iron-manganese alloy known as Hadfield metal is shown. This alloy is a very hard material. It is difficult to machine and due to the ease of oxidation of manganese, it is not produced in powder form by conventional melt methods. Lathe shavings of this material were ball milled and the metal powder, screened to 100/200 mesh. This powder had

some dehydrogenation activity prior to treatment but the effect of ammonia treatment as will be seen from the presented data effected a doubling of the dehydrogenation activity. A sample of pure manganese powder in the form of 100/200 mesh was also treated in accordance with Example 20 for purposes of comparison. The manganese was nitrified by the ammonia treatment, but it possessed no dehydrogenation activity.

Table III

Example	Metal powder, name	Metal alloyed with Fe, percent Mn	Ammonia treatment		Percent N in Metal	Dehydrogenation activity			
			Rate l./min.	Cc.H ₂ O/hr.		¾ hour		1¼ hours	
						Weight percent arom.	Weight percent liq. rec.	Weight percent arom.	Weight percent liq. rec.
18-----	Hadfield ¹ ----	10-14	None	None	-----	23	86	17	90
			0.9	7.5	6.3	42	71	39	79
19-----	do ² -----	10-14	None	None	-----	2	97	-----	-----
			0.7	8.2	3.0	25	88	19	90
20-----	Pure Mn ¹ ----	100	0.8	7.5	9.0	0	100	-----	-----

¹ Screened to 100/200 mesh powder.² Coarse lathe turnings.³ NH₃ treat at 40 p.s.i.g.

The activation process accomplished in the above examples is believed to be due to conversion of the nickel or manganese to a more accessible and perhaps strained condition due to the opening up of the iron lattice

nickel powder to commercial chromia-alumina, molybdena-alumina and molybdena-chromia-alumina catalysts. The effect of converting molybdena-alumina to a molybdenum nitride supported catalyst is also compared.

Table V

Example	Catalyst	Pretreatment	Surface area m. ² /g.	Dehydrogenation activity at 1½ hrs.	
				Weight percent arom.	Weight percent liq. rec.
23-----	Cr ₂ O ₃ /Al ₂ O ₃ (containing about 33 weight percent Cr ₂ O ₃ and 67 weight percent Al ₂ O ₃).	½ hr., H ₂ 850° F-----	219 fresh cat-----	2	100
24-----	MoO ₃ /Cr ₂ O ₃ /Al ₂ O ₃ (containing about 10 weight percent MoO ₃ , 30 weight percent Cr ₂ O ₃ and 60 weight percent Al ₂ O ₃).	do-----	138 fresh cat-----	8	100
25-----	do-----	2 hrs., H ₂ , 1,200° F-----	138 fresh cat-----	18	97
26-----	MoO ₃ /Al ₂ O ₃ (containing about 10 weight percent MoO ₃ and 90 weight percent Al ₂ O ₃).	½ hr., H ₂ , 850° F-----	145 fresh cat-----	4	100
27-----	do-----	2 hr., H ₂ , 1,200° F-----	do-----	9	98
28-----	do-----	2 hr., dry NH ₃ , 1,200° F-----	do-----	10	100
29-----	316 stainless steel powder-----	7 hr., wet NH ₃ , 1,200° F-----	<5 treated cat-----	46	92
30-----	Nickel powder-----	4 hr., wet NH ₃ , 1,200° F-----	do-----	40	95

caused by nitride formation. When pure nickel powder was treated with ammonia-steam under the same conditions as unexpected result occurred. Nickel nitride was not formed to any appreciable extent under the conditions of the specified ammonia treatment. However, an extremely high dehydrogenation activity was produced. Analysis of a sample of 100/200 mesh pure nickel powder which had been treated with ammonia-steam for 4 hours at 1200° F. showed less than 0.1 percent by weight of nitrogen. Data indicating the activation produced are set forth in Table IV below.

It will be seen from the foregoing data that the ammonia activated massive nickel and stainless steel catalyst obtained in accordance with the present invention possessed a substantially higher dehydrogenation activity than specified conventional catalysts.

In addition to providing an improved dehydrogenation catalyst, it is also within the purview of the present invention to use such a catalytic material as a suitable component of a dual function catalyst in petroleum conversion operations such as, for example, in reforming, isomerization, hydrocracking, aromatization, etc. Cata-

Table IV

Example	Nickel metal form	Ammonia treatment		Percent N in Metal	Dehydrogenation activity			
					¾ hour		1¼ hours	
		Rate l./min.	Cc.H ₂ O/ hr.		Weight percent arom.	Weight percent liq. rec.	Weight percent arom.	Weight percent liq. rec.
21-----	100/200 mesh powder-----	None----- 4 hrs. H ₂ at 1,200° F.	None----- 7.5	----- 0.08	1 1	89 100	----- 46	----- 98
		1.0----- 0.8-----	None----- 7.5	0.06-----	51 50	92 95	47	93
22-----	Wire .02" D x .02"-----	None----- 0.9-----	None----- 7.5	----- 0.05	0 14	100 98	----- 7	----- 100

It will be seen from Examples 21 and 22 that pure nickel both in the form of a fine powder as well as in the form of small pieces of wire underwent substantial dehydrogenation activation upon treatment with ammonia. The nickel in the form of finely divided powder showed a greater extent of activation due to the larger area of metal surface available. It is to be noted that in the case of pure nickel, addition of steam to the ammonia appears to afford little added benefit.

The data set forth in Table V compares the catalytic activities for dehydrogenation at 850° F. of ammonia-treated stainless steel powder and of ammonia-treated

lysts active for such conversion processes are known to require both an active dehydrogenation function and an acidic nature and it is known in the art that these two functions of the catalysts may be separate entities. The role of the dehydrogenation component is to furnish an olefin intermediate which is required in the reaction mechanism in order for the overall isomerization, cracking or aromatization reactions to occur. Mechanically mixed catalysts of powdered alumina and of iron-nickel powdered alloys have been made by dry pelleting the combined powders. The pellets (⅜" x ⅜") were then subjected to 4 hours of ammonia-steam treatment at

Table VI

Example	Catalyst composition	Ammonia treatment		Percent N in metal	Form cat. tested for DA	Dehydrogenation activity			
		Rate l./min.	Cc.H ₂ O/hr.			¾ hr.		1¼ hr.	
						Weight percent arom.	Weight percent liq. rec.	Weight percent arom.	Weight percent liq. rec.
31-----	60 weight percent metal alloy-----	None	None	-----	Pellets-----	1	100	-----	-----
32-----	do-----	0.9	7.5	6.3	do-----	48	88	45	91
33-----	do-----	1.0	7.5	6.8	do-----	44	91	42	95
34-----	do-----	1.0	7.5	6.8	Crushed pellets-----	52	93	49	98
35-----	77 weight percent metal alloy-----	None	None	-----	Metal powder equiv. weight-----	1	100	-----	-----
36-----	do-----	0.9	7.5	5.3	Crushed pellets-----	52	87	49	93
37-----	do-----	0.9	None	4.8	do-----	6	99	4	100

1200° F. in the same manner described previously for the metal powders. Because of the pelleting technique it was possible to use a finer mesh size of the metal powder than could be used when treating and testing powdered metal alone. The mixed catalyst shown in Table VI were made from 70 percent 200/325 plus 30 percent 325 mesh type 316 stainless steel powder containing 10 percent by weight nickel, 18 percent by weight chromium, 2 percent by weight molybdenum and remainder iron.

It will be seen from the foregoing data that the mechanically mixed composites likewise showed greatly enhanced dehydrogenation activity over composites which have not undergone the specified ammonia treatment. It is contemplated that in addition to powdered alumina other acidic components may likewise be employed such as for example, silica-alumina, silica-zirconia, silica-magnesia, and the like. It is also contemplated that the metal powder may be combined with the acidic material in any desired manner, for example by mixing the metal powder with hydrosols or hydrogels of alumina, silica-alumina, silica-zirconia, silica-magnesia or ternary combinations of the above or various other metal oxides.

We claim:

1. A process for imparting hydrocarbon dehydrogenation activity to a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese which comprises contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia containing water in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30.

2. A process for catalytically activating a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese which comprises contacting the same at a temperature between about 800 and about 1300° F. with an atmosphere of ammonia.

3. A process for catalytically activating a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese which comprises contacting the same in the form of particles having a size in the approximate range of 4 to 400 mesh, at a temperature between about 800 and about 1300° F. with an atmosphere of ammonia for a period of at least about ½ hour.

4. A process for catalytically activating a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese which comprises contacting the same in the form of particles having a size in the approximate range of 4 to 400 mesh, at a temperature between about 800 and about 1300° F. with an atmosphere of ammonia containing water in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30, for a period of at least about ½ hour.

5. A catalyst consisting essentially of a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, said catalyst having been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia containing water in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30.

6. A catalyst consisting essentially of a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, said catalyst having been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia for a period of at least about ½ hour.

7. A process for dehydrogenating a dehydrogenatable hydrocarbon which comprises contacting the same under dehydrogenating conditions with a catalyst consisting essentially of a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, said catalyst having been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia containing water in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30.

8. A process for dehydrogenating a dehydrogenatable hydrocarbon which comprises contacting the same under dehydrogenating conditions with a catalyst consisting essentially of a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, said catalyst having been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia for a period of at least about ½ hour.

9. A catalyst possessing both dehydrogenation and cracking activity consisting essentially of an intimate composite of an acidic oxide cracking component and a dehydrogenation component wherein said dehydrogenation component is a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, which has been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia containing water in an amount corresponding to a molar ratio of ammonia to water in the approximate range of 3 to 30.

10. A catalyst possessing both dehydrogenation and cracking activity consisting essentially of an intimate composite of an acidic oxide and a dehydrogenation component wherein said dehydrogenation component is a massive metal material selected from the group consisting of nickel, alloys comprising a major proportion of iron and a minor proportion of nickel, alloys comprising a major proportion of iron and a minor proportion of manganese, which has been activated by contacting the same at a temperature of between about 800 and about 1300° F. with an atmosphere of ammonia for a period of at least about ½ hour.

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