

[54] **DEHYDROGENATION AND DEHYDROCYCLIZATION METHOD**

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[58] Field of Search.....**260/683.3, 673.5**

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[57] **ABSTRACT**

A process for effecting a hydrogen transfer reaction involving the dehydrogenation of at least a part of the feed material, such as the dehydrocyclization of paraffinic hydrocarbons to produce aromatics, and the dehydrogenation of low molecular weight paraffins to produce hydrogen and monoolefins, including contacting the feed material with a catalyst comprising a metal of Group VIB of the Periodic System, in an amount between about 5 to 15 percent by weight of the finished catalyst, and a promotor of a metal of Group IV of the Periodic System, such as tin and lead in an amount of between about 1.0 and 10 percent by weight of the finished catalyst, both deposited on an inert oxide support such as gamma aluminas, silica-alumina, silica-magnesia, alumina-magnesia, etc., at a temperature between about 550° F. and 1,250° F., a pressure between about 0.01 and 2,600 mm. mercury absolute, and a liquid hourly space velocity between about 0.1 and 10. Where lower paraffins are dehydrogenated to olefins and hydrogen, the hydrogen is separated from the olefins and contacted with coal liquids in the presence of a hydrogenation catalyst, preferably of the same character as the dehydrogenation catalyst, and under conditions sufficient to a hydrogenate at least a part of the coal liquids. An additional promotor selected from the group of alkali metals, alkaline earth metals and rare earth metals may also be added.

10 Claims, No Drawings

DEHYDROGENATION AND DEHYDROCYCLIZATION METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a method for effecting reactions involving the dehydrogenation of organic materials. In a more specific aspect, the present invention relates to a method for the dehydrogenation and dehydrocyclization of hydrocarbon materials.

Numerous processes have been developed for the dehydrogenation of organic materials and, particularly, for the dehydrogenation and dehydrocyclization of non-aromatic hydrocarbons.

Among the dehydrocyclization type reactions are those involving the treatment of a variety of feedstocks containing normal paraffins. In these instances, normal paraffins, such as n-hexane and n-heptane, or mixtures thereof, are dehydrogenated and cyclized to produce aromatic hydrocarbons. This type reaction may also be applied to hydrocarbon mixtures containing normal paraffins, such as primary flash distillates and the products of the well-known reforming process in which a naphtha fraction is contacted at elevated temperature and pressure and in the presence of hydrogen with a dehydrogenation catalyst, for example a catalyst consisting essentially of platinum and alumina with or without combined halogen to produce a gasoline fraction of increased octane number. The dehydrocyclization reactions are, of course primarily confined to the treatment of materials having five carbon atoms and higher.

The dehydrogenation type of reaction without cyclization also is primarily applied to paraffinic hydrocarbons. However, in this case, the hydrocarbon feed is normally a hydrocarbon having five or less carbon atoms per molecule. Specifically, in this latter case, the petroleum industry now produces a wide variety of hydrocarbon streams for use as fuels and chemicals. Two of the more important chemicals are olefins which are utilized as chemical intermediates and hydrogen which is used for the production and processing of petrochemicals and fuels. At the present time, most of the unsaturated light hydrocarbons are obtained as by-products of cracking processes. While this is a relatively cheap source of light olefins, the purity of the product does not generally meet requirements where high purity is needed. One possible means of obtaining relatively pure, unsaturated hydrocarbons is by the dehydrogenation of the corresponding saturated hydrocarbons. This is a relatively simple operation. Large quantities of the raw material can be obtained at a reasonable price. Several processes have been developed for light paraffin dehydrogenation. These generally include cyclic, adiabatic, fixed-bed regenerative processes requiring short cycle times due to coke deposition on the catalyst. Therefore, for continuous operation, a minimum of three reactors is required with one reactor on-stream, one being regenerated, and one on standby. Multiples of this system can be utilized to increase olefin production. Another method for producing unsaturates is the pyrolysis of hydrocarbons. This is a process which is used almost exclusively for the production of acetylene, ethylene, and propylene. One drawback of this system is the high temperature required and the low purity of the hydrogen product stream. Yet another method which has been developed

entails the dehydrogenation of paraffins over precious metal catalysts. However, conversions are very low, about 10 percent, and olefin separation must be effected by aromatic alkylation. The production of hydrogen for the petroleum-petrochemical industry is generally through catalytic reforming of naphthas or the steam reforming of light hydrocarbons. The hydrogen available from catalytic reforming is rather limited and in short supply, so that more and more, producers are resorting to steam reforming of light hydrocarbons to satisfy the massive hydrogen requirements of today's operations.

Hydrogen requirements are also extremely high in processes for the treatment of liquids derived from coal. For example, coal liquids may be obtained from coal in solid form by carbonization or pyrolysis of the solid coal to produce coal tar products and the solvent extraction of coal solids with solvents, such as tetralin, decalin and the like, to produce a solvent extract. It is therefore highly desirable that an integrated process for the production of substantial volumes of hydrogen and the saturation and upgrading of coal liquids with such hydrogen be provided.

It is therefore an object of the present invention to provide a process for effecting reactions involving the dehydrogenation of organic materials. Another object of the present invention is to provide an improved process for effecting reactions involving the dehydrogenation or dehydrocyclization of organic materials. Yet another object of the present invention is to provide an improved process for the saturation of highly unsaturated organic materials derived from solids. Another and further object of the present invention is to provide an integrated process for the saturation of coal liquids including dehydrogenating paraffinic hydrocarbons to produce mono-olefins and hydrogen, separating the hydrogen from the mono-olefins and contacting the coal liquid with said hydrogen under hydrogenation conditions. It is also an object of the present invention to provide an improved process for the production of olefins and hydrogen. Yet another object of the present invention is to provide an improved process for the production of olefins and hydrogen by the dehydrogenation of paraffins. A further object of the present invention is to provide an improved process for the production of olefins and hydrogen by the dehydrogenation of paraffins which utilizes a novel catalyst system. A further object of the present invention is to provide an improved process for the conduct of dehydrogenation-type reactions which utilizes a catalyst capable of high conversion rates. Another and further object of the present invention is to provide an improved process for the conduct of dehydrogenation-type reactions which utilizes a catalyst of high selectivity. Still another object of the present invention is to provide an improved process for the conduct of dehydrogenation-type reactions which utilizes a catalyst having a low coking rate. These and other objects and advantages of the present invention will be apparent from the following detailed description.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, hydrocarbon materials are dehydrogenated by contact-

ing the hydrocarbon material with a metal of Group VI of the Periodic System and a promoter of Group IV of the Periodic System, and, if desired, an additional promoter selected from the group consisting of oxides of alkali metals, alkaline earth metals, rare earth metals, Group VIII metals and mixtures thereof.

Suitable feedstocks for use in the dehydrocyclization of non-aromatic hydrocarbons include those previously mentioned, such as n-hexane and n-heptane and mixtures of these, as well as hydrocarbon mixtures containing normal paraffins, such as distillates and products of reforming operations.

The dehydrocyclization operation may be carried out at temperatures varying all the way from 550° F. to about 1,150° F., at pressures between about 0.01 and 2,600 mm. mercury absolute, and at liquid hourly space velocities of from 0.1 to 10.

Suitable feedstocks for use in the dehydrogenation include ethane, propane, normal butane, iso-butane, normal pentane, iso-pentane, etc.

Processing conditions for the dehydrogenation reaction are dependent upon the feedstock employed. Generally, temperatures between about 900° F. and 1,250° F., pressures between about 100 and 2,500 mm. mercury absolute, and liquid hourly space velocities from about 0.1 to 10 may be employed. More specifically, if ethane is the feedstock, the temperature should be between about 1,100° F. and 1,250° F. Where C₃ to C₅ paraffins are the feedstock, a temperature of 900° to 1,150° should be used.

The separation of the monoolefins and hydrogen produced in the dehydrogenation reaction may be effected by selective adsorption and other known separation techniques. The separated hydrogen is then contacted with liquid materials of a highly unsaturated nature such as coal liquids derived from solid coal. For example, it is known that solid coal can be crushed or ground and subjected to carbonization or pyrolysis at elevated temperatures to produce liquid known as coal tar liquids. It is also known that crushed or pulverized coal can be contacted with a suitable solvent, at slightly elevated temperatures, such as tetralin, decalin and other hydrogen transfer solvents, to thereby produce a solvent extract which resembles coal tar liquids or heavy petroleum crudes. Both of these crude materials, particularly the solvent extracts, are highly unsaturated mixtures containing substantial volumes of cyclic compounds, which must be saturated to some extent before they can be further processed to produce fuels and chemicals. Such saturation is effected in accordance with the present invention by contacting the coal liquids with the hydrogen separated from the monoolefins and recovering the hydrogenated coal liquids. The hydrogenated coal liquids then resemble in substantially all respects, except for aromaticity, hydrocarbon liquids derived from petroleum crude oils; and, accordingly, they may be processed in accordance with conventional refinery practices for the conversion of petroleum oils.

The hydrogenation of the coal liquids may be carried out in the presence of the same catalysts employed for the dehydrogenation reaction. However, any known hydrogenation catalysts may also be employed, such as Group VIII metals, for example, platinum, palladium, rhodium and nickel and cobalt and Group VI metals,

such as molybdenum or tungsten or various combinations of these metals, deposited on a carrier such as alumina or silica. Hydrogenation conditions may include temperatures from about 450° to 800° F., preferably about 500° to 800° F., pressures of about 400 to 10,000 psig., liquid hourly space velocities from about 0.1 to 10, and hydrogen-to-hydrocarbon mole ratios from about 1 to 20 to 1.

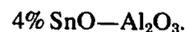
The novel catalysts of the present invention include an active metal from Group VIB of the Periodic System, and specifically, chromium, molybdenum and tungsten, in a concentration of about 5 to 15 percent by weight based on the finished catalyst. The promoter of the present invention includes a Group IV metal, in its oxide form, and if desired, alkali metals, such as potassium, rubidium and cesium, alkaline earth metals, such as calcium, strontium and barium, Group VIII metals, such as platinum, rhodium, ruthenium, palladium and nickel, and rare earth metals, such as cerium or thorium in a concentration of about 1 to 10 percent by weight based on the finished catalyst product. The promoter is preferably in its oxide form. Both of these materials are deposited on an inert oxide support, preferably an alumina of a gamma type, such as the bayerite, beta, etc., and boehmite crystalline forms. Other suitable supports of this character may be used also, such as other aluminas, silica-alumina, silica, silica-magnesia, alumina-magnesia, silica-zirconia, etc.

The catalysts may be prepared by techniques well known in the art. For example, such preparation includes known impregnation techniques. One can employ extrudates or pellets for impregnation or powders followed by pelletization or extrusion to yield the finished catalyst. The active metal and the promoter are added through the use of water-soluble salts, such as their halides, nitrates, sulfates, acetates, etc. Easily hydrolyzed salts can be kept in solution without decomposition by employing the appropriate inorganic acids. Well-known procedures for drying and calcination of the catalysts may also be employed, such as vacuum drying and calcination in oxidative, neutral and reductive atmospheres, utilizing calcination temperatures of about 800° to 1,200° F.

The following examples illustrate the preparation of the catalysts of this invention.

EXAMPLE I

To 900 ml. of distilled water was added 81 g. of stannous sulfate and 30 ml. of concentrated sulfuric acid. The sulfuric acid was required to bring the insolubles from the stannous sulfate into solution. This was believed to be tin hydroxide. This solution was added to 900 ml. of a boehmite alumina as pellets and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250° F. for 1 hour and calcined in air at 950° F. for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:



A solution containing 150 ml. of distilled water, 45 g. of chromic acid, and 9.5 g. of potassium nitrate was added to 150 ml. of 4% SnO—Al₂O₃ pellets from above. Catalyst and solution was in contact for 15

minutes and the unadsorbed liquid was decanted. The resulting catalyst was dried at 250° F. for 1 hour and calcined in air at 950° F. in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

15% Cr₂O₃—2% K₂O—4% SnO—Al₂O₃.

EXAMPLE II

To 600 ml. of distilled water was added 20 g. of lead nitrate. This solution was added to 600 ml. of a boehmite alumina as pellets and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250° F. for 1 hour and calcined in air at 950° F. in a muffle furnace for 16 hours. This yielded a catalyst of the following composition:

2% PbO—Al₂O₃.

A solution containing 150 ml. of distilled water, 36 g. of chromic acid, and 5.5 g. of cesium nitrate was added to 150 ml. of 2% PbO—Al₂O₃ pellets from above. Catalyst and solution was in contact for 15 minutes and the unadsorbed liquid was decanted. The resulting catalyst was dried at 250° F. for 1 hour and calcined in air at 950° F. for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:

12% Cr₂O₃—2% Cs₂O—2% PbO—Al₂O₃.

EXAMPLE III

By employing the techniques and procedures outlined in Examples I and II other catalytic compositions were prepared. A solution containing 600 ml. of distilled water, 54 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid was added to 600 ml. of a boehmite alumina. Drying and calcination yielded the following composition:

3% SnO—Al₂O₃.

A solution containing 150 ml. of distilled water, 29 g. of ammonium molybdate, 10 g. of potassium nitrate, and 5 ml. of concentrated ammonium hydroxide was added to 150 ml. of 3% SnO—Al₂O₃ pellets. Drying and calcination yielded the following composition:

12% MoO₃—2% K₂O—3% SnO—Al₂O₃.

EXAMPLE IV

To 600 ml. of distilled water was added 54 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid. The tin sulfate was partially insoluble and the sulfuric acid brought it into solution. This insolubility was probably due to the presence of tin hydroxide. This solution was added to 600 ml. of a boehmite alumina and after contact for 15 minutes, the unadsorbed liquid was decanted from the catalyst pellets. The resulting impregnated catalyst was dried at 250° F. for 1 hour and calcined at 950° F. for 16 hours to yield a catalyst of the following composition:

4% SnO—Al₂O₃.

A solution containing 150 ml. of distilled water and 30 g. of chromic acid was added to 150 ml. of 4% SnO—Al₂O₃ pellets (prepared as above) and allowed to

remain in contact for 15 minutes before decanting the unadsorbed liquid. The impregnated catalyst was dried at 250° F. for 1 hour and calcined in air at 950° F. for 16 hours in a muffle furnace. This yielded a catalyst of the following composition:

10% Cr₂O₃—4% SnO—Al₂O₃.

EXAMPLE V

A 4% SnO—Al₂O₃ catalyst was prepared according to the procedure described in Example IV. To 150 ml. of 4% SnO—Al₂O₃ pellets was added a solution containing 150 ml. of distilled water and 1 g. of rhodium trichloride. The unadsorbed liquid was decanted and the catalyst dried and calcined according to the procedure outlined in Example I. To the rhodium oxide-tin oxide-alumina catalyst was added a solution containing 150 ml. of distilled water and 45 g. of chromic acid. The catalyst was dried and calcined (see Example I) to yield the following composition:

15% Cr₂O₃—0.5% Rh—4% SnO—Al₂O₃.

EXAMPLE VI

To 400 ml. of distilled water was added 18 g. of stannous sulfate. This solution was added to 200 ml. of bayerite alumina (similar to beta) and 200 ml. of boehmite alumina in separate impregnation vessels. The solution remained in contact with the aluminas for 15 minutes and was then decanted. The resulting catalysts were dried for 1 hour at 250° F. and calcined in air in a muffle furnace for 16 hours at 950° F. This yielded two 4 percent tin oxide on alumina catalysts. To each tin oxide-alumina catalyst was added a solution containing 200 ml. of distilled water and 40 g. of chromic acid. The solution and catalyst remained in contact for 15 minutes and the remaining solution removed by decantation. The catalyst was dried at 250° F. for 1 hour and calcined in air in a muffle furnace for 16 hours at 950° F. This yielded the following composition:

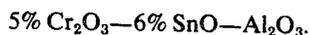
10% Cr₂O₃—2% SnO—Al₂O₃.

EXAMPLE VII

To 600 ml. of a boehmite alumina was added a solution containing 600 ml. of distilled water, 80 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid. The stannous sulfate was not completely water soluble and the sulfuric acid dissolved all insolubles to give a clear solution. The insolubles are believed to be tin hydroxide which are converted to the soluble sulfate. These insolubles were not noted in Example I. The solution and catalyst remained in contact for 15 minutes and the remaining solution then removed by decantation. The catalyst was dried at 250° F. for 1 hour and calcined in air in a muffle furnace for 16 hours at 950° F. This yielded a 6 percent tin oxide on alumina catalyst.

To 150 ml. of 6 percent tin oxide on alumina pellets was added a solution containing 150 ml. of distilled water and 15 g. of chromic acid. The solution and catalyst remained in contact for 15 minutes and the unadsorbed solution removed by decantation. The catalyst was dried at 250° F. for 1 hour and calcined in

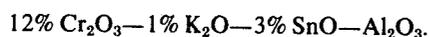
air in a muffle furnace for 16 hours at 950° F. This yielded the following composition:



EXAMPLE VIII

To 600 ml. of distilled water was added 54 g. of stannous sulfate and 20 ml. of concentrated sulfuric acid. The stannous sulfate was not completely water soluble and the sulfuric acid dissolved all insolubles to give a clear solution. The insolubles are believed to be tin hydroxide which are converted to the soluble sulfate. The solution was added to 600 ml. of boehmite alumina extrudate. The solution and catalyst remained in contact for 15 minutes and the unadsorbed solution was removed by decantation. The catalyst was dried at 250° F. for 1 hour and calcined in air in a muffle furnace for 16 hours at 950° F. This yielded a 3 percent tin oxide on alumina catalyst.

To 300 ml. of 3 percent tin oxide on alumina pellets was added a solution containing 300 ml. of distilled water and 10 g. of potassium nitrate. The solution and catalyst remained in contact for 15 minutes and the unadsorbed liquid was removed by decantation. The catalyst was dried at 250° F. for 1 hour and calcined in air in a muffle furnace for 16 hours at 950° F. This yielded the following composition:



The following Tables illustrate the present invention.

TABLE I

FEED: Propane

Conditions: 1110° F, 810 mm. Hg absolute, 5 LHSV.

Run	1		2		3	
	Commercial					
	12Cr ₂ O ₃ -2MgO-Al ₂ O ₃		10Cr ₂ O ₃ -4SnO-Al ₂ O ₃		10Cr ₂ O ₃ -2K ₂ O-2SnO-Al ₂ O ₃	
Catalyst						
Time - Min.	11	88	11	88	11	88
Conversion	37.2	12.5	28.8	26.1	31.2	30.5
Product Dist.						
Mole %:						
H ₂	27.8	14.7	22.4	20.9	22.2	22.0
Methane	4.0	1.6	1.5	1.4	1.8	1.7
Ethane	3.2	2.1	1.5	1.4	1.7	1.4
Dry Gas						
Concentration:						
H ₂	80	80	88	88	87	88
Methane	11	9	6	6	7	7
Ethane	9	11	6	6	6	5

TABLE II

Feed: Propane

Conditions: 1110° F, 810 mm Hg absolute, 5 LHSV

Run	4	5	9	10	8	11	12
Catalyst	Commercial						
Chromia	12	10	10	10	15	15	15
Potassia	2MgO	2	—	2	4	—	4
Tin Oxide	—	—	2	2	—	4	2
Conversion	25.3	38.3	30.7	31.4	32.5	28.7	29.5
Selectivity	88.8	90.4	91.7	93.6	90.7	90.8	93.7
ΔConversion	24.7	6.0	7.4	0.79	18.4	2.9	0.6
Gm. Carbon/ 20 g. Catalyst	0.77	1.31	1.23	0.36	1.23	0.44	0.14

As shown in Table II, the data derived from catalysts combining the promoters (potassia and tin oxide) are not the average values one expects to obtain by summation of results obtained from catalysts utilizing each promoter separately. Instead, a synergistic effect is observed which produces a highly selective catalyst with excellent coke inhibiting properties and very little deactivation. This may be attributed to the formation of a completely different promoter, e.g., potassium stannate, potassium tin chromate, etc.

The superior performance achieved with chromia-potassia-tin oxide on alumina led to a study on the effect of potassia concentration, holding chromia and tin oxide constant.

TABLE III

Feed: Propane

Conditions: 1110° F, 810 mm Hg absolute, 5 LHSV

Run	13	14	15	16	17	18
Catalyst						
Chromia	10	10	10	12	12	12
Potassia	1	2	4	2	3	5
Tin Oxide	2	2	2	2	2	2
Conversion	32.1	31.4	20.3	31.0	29.5	27.5
Selectivity	93.7	93.6	90.8	94.7	94.3	95.1
ΔConversion	4.5	0.8	0	2.3	1.8	2.1
Gm. Coke/ 20 g. Catalyst	0.25	0.36	0.19	0.19	0.11	0.27

The data establishes that a balance must be maintained between the three components. At the 10 percent chromia level, this balance is approximated at 2 percent potassia and 2 percent tin oxide. A slightly higher average conversion with 1 percent potassia hardly justifies its higher rate of deactivation. The composition utilizing 4 percent potassia has catalyst fouling properties; however, low conversion and selectivity indicates an overload effect which inhibits dehydrogenation activity. At the 12 percent chromia level, the conversion drops as potassia concentration on catalyst is increased from 2 to 5 percent. With respect to catalyst fouling, 3 percent potassia is near optimum.

Thus, if the amount of tin oxide on the catalyst is

held constant, an increase in chromia content must be accomplished by an increased potassia concentration to achieve desirable performance.

A series of compositions were also prepared to determine the ideal tin oxide concentration. The results with these catalysts are shown in Table IV.

TABLE IV

Feed: Propane

Conditions: 1110°F, 810 mm Hg absolute, 5 LHSV

Run	19	20	21	22
Catalyst				
Chromia	10	10	12	12
Potassia	2	2	3	3
Tin	2	4	1	2
Conversion	31.4	26.3	36.4	29.5
Selectivity	93.6	94.1	94.6	94.3
ΔConversion	0.8	1.8	4.7	1.8
Gm. Coke/ 20 g. Catalyst	0.36	0.16	0.38	0.11

There is little advantage to going to higher than 2 percent tin oxide with the 10 chromia - 2 percent potassia composition. The additional tin oxide minimizes carbon on catalyst and improves selectivity; however, lower conversion and greater deactivation rate indicates the catalyst is unable to withstand much fouling. In the 12 percent chromia - 3 percent potassia, a definite improvement in catalyst life is observed with 2 percent tin oxide as opposed to 1 percent. The general trend with the data in Table V and the other tables indicates little incremental performance with greater than 2 percent tin oxide on catalyst.

In all catalysts tested, higher conversions are obtained with increased temperatures accompanied by poorer selectivities, greater coke laydown on catalyst, and consequently higher deactivation rates.

Increased yield is also achieved at lower space velocities.

In addition, selectivities decreased slightly while the change in conversion with time and carbon on catalyst deposition rates became nil.

Data was compiled to determine stability characteristics of these compositions. This included aging and regeneration properties. These catalysts were processed and regenerated with air for many cycles without any loss in initial and final activities. The commercial catalyst deactivated at a very rapid rate, while the catalyst compositions of this invention have a very shallow deactivation slope.

Other combinations are shown in Table V.

TABLE V

Feed: Propane

Conditions: 1110°F, 810 mm Hg absolute, 5 LHSV

Run	23	24	25	26	27	28
Catalyst	Commercial					
Metal Oxide	12Cr	15Cr	12Mo	12Cr	12Cr	10Cr
Promoter 1	2MgO	2Cs	2K	2K	2Cs	2Pb
Promoter 2	—	2Sn	3Sn	2Pb	2Pb	2Sn
Conversion	25.3	33.6	11.2	33.9	34.9	28.4
Selectivity	88.8	93.2	73.9	92.8	90.9	93.1
ΔConversion	24.7	2.9	5.0	11.8	11.2	3.8
Gm. Coke/ 20 g. Catalyst	0.77	0.41	1.09	0.90	1.28	0.93

The results in Table V show that molybdena can be substituted for chromia; however, a lower activity catalyst is obtained. As to promoter 1, any alkali metal oxide, alkaline earth metal oxide, or rare earth metal oxide can be utilized without a decrease in conversion or selectivity. Tin oxide or lead oxide are interchangeable.

When reference is made herein to the Periodic System of elements, the particular groupings referred to are as set forth in the Periodic Chart of the Elements, in "The Merck Index," Seventh Edition, Merck & Co., Inc., 1960.

We claim:

1. A process for dehydrogenating hydrocarbons predominating in aliphatic, paraffinic hydrocarbons having up to five carbon atoms per molecule comprising: contacting the hydrocarbons with a catalyst consisting essentially of about 5 to 15 percent by weight of a metal of Group VI of the Periodic System and about 1.0 to 10 percent by weight of a metal selected from the group consisting of lead oxide and tin oxide, both impregnated on an inert oxide support, under conditions sufficient to effect said dehydrogenating reaction, including, a temperature of about 550° to 1,250° F., a pressure of about 0.01 to 2,600 mm of mercury and a liquid hourly space velocity of about 0.1 to 10.

2. A process in accordance with claim 1 wherein the inert oxide support is a gamma alumina.

3. A process in accordance with claim 1 wherein the hydrocarbon is ethane and the temperature is about 1,100° to 1,250° F.

4. A process in accordance with claim 1 wherein the hydrocarbons contain three through five carbon atoms per molecule and the temperature is about 900° to 1,150° F.

5. A process in accordance with claim 1 wherein the paraffins are converted to hydrogen and olefins, the hydrogen and olefins are separated and coal liquids are contacted with the hydrogen in the presence of a hydrogenation catalyst and under conditions sufficient to hydrogenate at least a portion of said coal liquids.

6. A process in accordance with claim 5 wherein the hydrogenation catalyst is a catalyst of the same character as the dehydrogenation catalyst.

7. A process for dehydrogenating hydrocarbons predominating in aliphatic, paraffinic hydrocarbons having up to five carbon atoms per molecule comprising: contacting the hydrocarbons with a catalyst consisting essentially of about 5 to 15 percent by weight of a metal of Group VI of the Periodic System, about 1.0 to 10 percent by weight of a metal selected from the group consisting of lead oxide and tin oxide and about 1.0 to about 10 percent of a second promoting metal selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals and mixtures thereof, all impregnated on an inert oxide support, under conditions sufficient to effect said dehydrogenating reaction, including, a temperature of about 550° to 1,250° F., a pressure of about 0.01 to 2,600 mm of mercury and a liquid hourly space velocity of about 0.1 to 10.

8. A process in accordance with claim 7 wherein the second promoter is an alkali metal.

9. A process in accordance with claim 7 wherein the second promoter is an alkaline earth metal.

10. A process in accordance with claim 7 wherein the second promoter is a rare earth metal.