United States Patent

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[72] Inventors **Charles R. Noddings**
Midland;
Andrew J. Dietzler, Midland; Ronald G. Gates, Breckenridge, all of Mich.

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[73] Assignee **The Dow Chemical Company**
Midland, Mich.

Continuation-in-part of application Ser. No. 553,661, May 31, 1966, now abandoned, and a continuation-in-part of 604,661, Dec. 27, 1966, now Patent No. 3,409,701, dated Nov. 5, 1968, which is a continuation-in-part of application Ser. No. 335,810, Jan. 6, 1964, now abandoned, and a continuation-in-part of 335,841, Jan. 6, 1964, now abandoned, and a continuation-in-part of 335,775, Jan. 6, 1964, now abandoned, and a continuation-in-part of 335,784, Jan. 6, 1964, now abandoned. The portion of the term of the patent subsequent to Nov. 5, 1985, has been disclaimed.

[54] **METHOD FOR DEHYDROGENATING AND CRACKING ALKANES AND OLEFINS**
7 Claims, No Drawings

[52] **U.S. Cl.** ..... **260/678,** 252/437, 260/680 R, 260/683 R, 260/683.3
[51] **Int. Cl.** **C07c 3/32,** C07c 5/18
[50] **Field of Search** 260/680, 678, 683, 683.3; 252/437

[56] **References Cited**

UNITED STATES PATENTS

3,198,848	8/1965	Happel et al.	260/680 X
3,270,085	8/1966	Noddings et al.	260/683.2
3,409,701	11/1968	Noddings et al.	260/683.3 X

Primary Examiner—Paul M. Coughlan, Jr.
Attorneys—Griswold & Burdick, C. E. Rehberg and Glwynn R. Baker

ABSTRACT: Aliphatic hydrocarbons are dehydrogenated and/or cracked using catalysts prepared by precipitating nickel with a phosphate ion or coprecipitating chromium and nickel with phosphate ions, the latter coprecipitation being carried out to produce a material having from six to 12 atoms of chromium per atom of nickel on one hand or six to 12 atoms of nickel per atom of chromium on the other hand. The catalyst is precipated in the gel form in the presence of ammonium hydroxide.

METHOD FOR DEHYDROGENATING AND CRACKING ALKANES AND OLEFINS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of our copending application, Ser. No. 604,661 entitled "Catalyst and Method for Dehydrogenating and Cracking Alkanes and Olefins" filed Dec. 27, 1966 by Charles R. Noddings, Andrew J. Dietzler and Ronald G. Gates, now U.S. Pat. No. 3,409,701 granted Nov. 5, 1968, which in turn is a continuation-in-part of our then copending and now abandoned applications, Ser. No. 335,810 entitled "Nickel Chromium Phosphate Catalyst and Method for Dehydrogenating and Cracking Alkanes and Olefins," filed Jan. 6, 1964, filed by Charles R. Noddings, Andrew J. Dietzler and Ronald G. Gates; Ser. No. 335,841 entitled "Nickel Chromium Phosphate Catalyst and Method for Dehydrogenating and Cracking Alkanes and Olefins," filed by Charles R. Noddings and Ronald G. Gates, filed Jan. 6, 1964; Ser. No. 335,775 entitled "Nickel Phosphate Catalyst and Method for Dehydrogenating and Cracking Alkanes and Olefins," filed Jan. 6, 1964, by Charles R. Noddings and Ronald G. Gates; Ser. No. 335,784 entitled "Chromium Nickel Phosphate Catalyst and Method for Dehydrogenating and Cracking Alkanes and Olefins," filed Jan. 6, 1964, filed by Charles R. Noddings and Ronald G. Gates; and a continuation-in-part of Ser. No. 553,661 entitled "Method for Converting Propylene to More Valuable Products," filed May 31, 1966, by Charles R. Noddings, now abandoned.

BACKGROUND OF INVENTION

It is, of course, well-known that aliphatic hydrocarbons, e.g., petroleum fractions (mixed hydrocarbons) or individual paraffins or olefins, can be pyrolyzed to obtain a mixture of products comprising a small, though appreciable, proportion of conjugated diolefins and a larger proportion of shorter chain length unsaturated products. During such pyrolysis, it has been observed that several different kinds of reactions usually occur simultaneously, e.g., (1) dehydrogenation, (2) cracking of the carbon-to-carbon linkages in the molecule to form products containing fewer carbon atoms per molecule than the original hydrocarbon, and (3) polymerization of unsaturated hydrocarbons, so that the product is, in most instances, a hydrocarbon mixture. An example of such products is cracked-oil gas, containing paraffinic hydrocarbons ranging in chain length from methane to hexane, olefins ranging in chain length from ethylene to hexylene, and a small amount, usually less than 10 percent, of less saturated hydrocarbons such as butadiene, isoprene, piperylene and acetylenic hydrocarbons. The difficulties involved in recovering the more useful products from such mixture add greatly to their cost.

It is an object of this invention to provide a catalyst for the dehydrogenation and/or cracking of C_3 and higher hydrocarbons, and particularly C_4 and higher hydrocarbons. Another object of the present invention is to provide a method wherein the new catalyst will produce useful organic products (that is products other than CO_2, carbon and hydrogen) from the pyrolysis, (i.e., cracking and/or dehydrogenation) in quantities which increase the economical value of the starting carbon compounds. A further object is to provide a set of operating conditions under which the new catalysts may effectively be used for the foregoing purposes. Other objects will be apparent from the following description of the invention.

SUMMARY OF INVENTION

We have found that a nickel phosphate, chromium-nickel phosphate containing an average of between six and 12 and preferably from about six to about nine atoms of chromium per atom of nickel or nickel-chromium phosphate containing an average of between six to 12 atoms and preferably six to about nine atoms of nickel per atom of chromium, and each of which is precipitated under a pH from 4 to about 10 is, under certain operating conditions, effective in catalyzing the thermal dehydrogenation and/or cracking of C_3 and higher hydrocarbons, and particularly C_4 and higher hydrocarbons, to C_2 and C_3 hydrocarbons, containing a high proportion of olefins.

Further in accordance with the present invention, it has been found that propylene can be converted to a more valuable product by simultaneously cracking a portion of the propylene to ethylene and dehydrogenating a considerable proportion to propadiene and propyne by passing 100 to 300 volumes of the propylene per volume of catalyst per hour (S.T.P. space velocity) in admixture with between about 10 and 30 volumes of steam at between about 700° C. and 900° C. over a coprecipitated chromium-nickel phosphate catalyst having either 6 to 9 moles of chromium per mole of nickel or 6 to 9 moles of nickel per mole of chromium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The catalysts are prepared by mixing together water-soluble salts of nickel and/or chromium in the appropriate ratios, with a water-soluble source of the ortho-phosphate ion (PO_4) in an aqueous medium under conditions such that the pH is within the range specified above for the particular embodiment. Material of good catalytic quality is obtained when a two metal phosphate, that is when the chromium and nickel are employed to provide from 6 to 12 moles of chromium per mole of nickel or nickel per mole of chromium. Further, while not critical but desirable, the phosphate moiety is employed in a slight excess over that which is theoretically necessary to combine with the metal ions to form a metal orthophosphate. It is to be understood that the pH may, but does not have to be maintained at that which produces the catalytically operative material during mixing but can be adjusted, after mixing and precipitation, but before setting, by addition of a base or acid as necessary to the reaction mixture to bring the solution within the desired range of pH set forth for preparation of a material capable of catalytically dehydrogenating and/or cracking hydrocarbons.

The contacting and mixing of the reactants in accordance with the above recitation can be carried out in several manners, such as simultaneously, stepwise or intermittently, each in either a batchwise or continuous manner.

Examples of salts which may be used as starting materials in preparing the catalyst are the chlorides, bromides, nitrates, and acetates, etc., of chromium and nickel. Examples of water-soluble phosphates that may be employed as starting materials are phosphoric acid, disodium phosphate, trisodium phosphate, dipotassium phosphate, a diammonium phosphate, etc.

The catalyst can also be prepared in either a batchwise manner or a continuous manner by feeding separate streams of:

1. a base, preferably aqueous ammonia and in the case of nickel phosphate, some ammonium ion must be present, although other bases can be employed when preparing the double metal salts, as well as mixtures of two or more different bases;

either a single or as separate streams

2. an aqueous solution of nickel or chromium and nickel salts (in relative proportions corresponding to between six and 12 and preferably about six to nine atoms of chromium per atom of nickel or between six and 12 and preferably six to nine atoms of nickel per atom of chromium;)

and either a separate or as a part of any one of the aforesaid streams

3. a dissolved orthophosphate, into a reaction chamber. The relative rates of flow are adjusted so that the resultant mixture will achieve, continuously or upon completion of the mixing, a pH of 4 to 10 when a dehydrogenation catalyst is desired of the chromium-nickel class, 7 to 10 when the nickel-chromium class is produced, 4 to 9 when nickel phosphate class is produced, and 5 to 7 when a

cracking catalyst of the nickel-chromium class is desired. It is desirable to retain within the reaction zone a portion of the precipitated phosphate which forms, this then being blended with succeeding portions or batches. This is conveniently achieved by adjusting the outflow of the precipitated phosphate to retain a portion of the flocculent material in the reaction vessel. The reaction mixture, or preferably the settled lower layer thereof, may be filtered to obtain a filter cake which contains 2 to 10 percent or more, usually about 22 percent of the precipitated phosphate.

The phosphate precipitated from a mixture of higher pH value which is then adjusted to the pH above set forth for the particular catalyst is of good catalytic activity, but is extremely slow in settling. The phosphate from a mixture of pH value below 4 settles rapidly, but is less active as a catalyst for the cracking and dehydrogenation of C_4 hydrocarbons that is phosphate precipitated from mixtures within the range of pH values set forth. Usually water is employed as the solvent for the starting materials, but other ionizing solvents, e.g., aqueous alcohol, may in some instances be used.

In any event after the reaction is complete and the desired pH obtained the precipitate is separated from the liquor by filtration or decantation and is washed with water decanting or filtering after each washing. The washing should be carried out so as to remove as thoroughly as possible readily soluble compounds from the product, since such impurities have a disturbing and erratic action on the thermal decomposition of hydrocarbons. Of particular attention are the unreacted chlorides or byproduct chlorides which, if retained in the catalyst, tend to deactivate the latter. The catalyst is, at this stage in its preparation, a solid or gellike substance which is apparently amorphous.

After being washed with water, the product is dried, usually at temperatures between 60° and 150° C. The dried product is a hard gel usually of greenish color. The gel may be crushed or otherwise reduced to granules, or small lumps, and be used directly as a dehydrogenation catalyst. However, it is preferably pulverized, e.g., to a particle size capable of passing a 28-mesh screen, and the powdered product is treated with a lubricant and is pressed into the form of pills, tablets, or granules of size suitable for use as a catalyst, e.g., into the form of tablets of from one-sixteenth to one-half inch diameter. The lubricant serves to lubricate the particles during the operation of pressing them into pills and its use permits the formation of pills of greater strength and durability than are otherwise obtained. As the lubricant we preferably use a substance capable of being removed by vaporization or oxidation from the product, e.g., a substance such as graphite, a vegetable oil, or a hydrocarbon oil, etc.

C_4 and higher hydrocarbons can be cracked and/or dehydrogenated in the presence of steam and the catalysts of the present invention at temperatures between 600° and 750° C., and in some instances at temperatures as much as 50° C. below or above this range. The reaction is advantageously carried out at temperatures between 650° and 700° C.

Following the procedure of the present invention it is possible to obtain commercial yields of propyne and propadiene from propylene when a propylene-rich feed is contacted with a chromium-nickel (6-9 Cr/Ni) or nickel-chromium (6-9 Ni/Cr) phosphate at between 700° C. and 1,000° C.

Except for the foregoing limitations, the conditions under which the dehydrogenation reaction is carried out may be varied widely. Also, the method is operable at atmospheric, subatmospheric, or at superatmospheric pressures, provided the hydrocarbon reactant is in vaporized form. In some instances, the yield of dehydrogenated product decreases upon increase of the reaction pressure above atmospheric. However, the ability to operate at an increased pressure is of considerable advantage, since condensation of the reaction products may thereby be facilitated. In general, the proportion of hydrocarbon reacted and also the amount of byproduct formation per pass through the catalyst bed tend to decrease with increase in the rate of vapor flow, and vice versa.

In producing cracked and dehydrogenated hydrocarbon products in accordance with the invention, a reaction chamber is charged with the catalyst and the lubricant, if employed, is removed from the catalyst. This is usually accomplished by passing an O_2-containing gas such as oxygen or air, preferably a mixture of about equal volumes of air and steam, through the catalyst bed at a high temperature, e.g., 450° to 750° C. When the lubricant used in preparing the catalyst granules is a substance capable of being vaporized, e.g., a mineral or vegetable oil, the step of treating the catalyst with air may be preceded by one of passing an inert gas or vapor such as steam, nitrogen, or carbon dioxide over the catalyst so as to vaporize at least a portion of the binding agent from the catalyst granules.

After freeing the catalyst of the lubricant, the catalyst bed is swept free of the O_2 or air with steam and is heated to the desired reaction temperature, preferably by passing superheated steam through the same. A mixture of steam and the hydrocarbon reactant, e.g., propane, butylene, amylene, hexylene, butane, pentane, or hexane, having at least three carbon atoms, is then passed through the catalyst bed at a temperature between 600° and 900° C., and preferably between 650° and 700° C. The usual procedure is to pass the hydrocarbon gas into admixture with steam which has been superheated to 750° C. or above, i.e., to a temperature sufficient so that the resultant mixture is at the desired reaction temperature, and to pass the mixture through the bed of catalyst. However, the heat may be supplied in other ways, e.g., by forming the steam and hydrocarbon mixture at a lower temperature and passing the mixture through a preheater to bring it to the desired temperature, or by externally heating the catalyst chamber itself. The yield of olefins is usually highest when from 10 to 20 volumes of steam are employed per volume of the gaseous or vaporized hydrocarbon, but the steam may be used in smaller or larger proportions if desired. As hereinbefore mentioned, the rate of vapor flow through the catalyst chamber may be varied widely, but in practice the flow usually corresponds to between 100 and 700 liters of the hydrocarbon (expressed as at 0° C. and 760 millimeters pressure) per liter of catalyst bed per hour.

The vapors issuing from the catalyst chamber are ordinarily passed through heat exchangers to condense first the water and then the hydrocarbon products. By repeatedly recycling the unreacted hydrocarbons, a cracked or dehydrogenated product may be produced in a 60 percent yield or higher and usually in a yield of from 70 to 75 percent of theoretical or higher.

During use in the process, the catalyst gradually accumulates a small amount of carbon, or nonvolatile organic material, and loses its activity. Accordingly, flow of the hydrocarbon starting material is periodically interrupted and air, admixed with steam, is blown through the catalyst bed, e.g., at temperatures between 450° and 700° C., and preferably at the hydrocarbon reaction temperature, to oxidize and remove the carbonaceous material and thus reactivate the catalyst. Usually from 10 to 30 minutes are required to carry out this reactivation step. However, if, during compounding of the catalyst into tablet form, an agent having the property of catalyzing the oxidation of carbon is admixed therewith, the time subsequently required for reactivating the catalyst with steam and air may be reduced markedly. For instance, the incorporation of one or two percent by weight of chromic oxide in the catalyst tablets facilitates reactivation of the catalyst. Other agents having the property of catalyzing the burning of carbon are known to the art.

After completing the reactivation step, the catalyst chamber is again swept free of air with steam and the introduction of hydrocarbons, together with the steam, is resumed. Usually, reactivation of a catalyst is advisable after from 15 to 60 minutes of use in the dehydrogenation reaction. In practice, two or more catalyst chambers are preferably employed in a system provided with connections for passing the reaction mixture alternately through different catalysts beds. One catalyst bed is usually employed in the reaction while another

is being reactivated. By operating in this manner, the reaction may be carried out continuously.

The following examples illustrate the present invention, but are not to be construed as limiting:

EXAMPLE 1

Chromium chloride, 14.3 gram moles, as an 11.5 weight percent aqueous solution thereof was mixed in a vessel with 2.38 gram moles of nickel chloride as a 29 weight percent aqueous solution and 16.3 gram moles of phosphoric acid as a 71 weight percent aqueous solution and the resulting mixture was diluted with water to a total volume of 80 gallons. Upon completion of the addition of the above-enumerated chemicals to the vessel reactor, 49.1 gram moles of an aqueous 14.7 weight percent ammonium hydroxide solution were slowly added with stirring over 2.5 hours of reaction at which time the pH remained constant at 4.5. The reaction was considered complete when the pH remained constant. Thereafter, the reaction mass was allowed to settle overnight, after which the supernatant liquid was drawn off (approximately 58 gallons decanted) and the resulting thick slurry filtered and washed with water. The filtrate was discarded. In this specific instance the slurry was washed by decantation with water 14 times until chloride free, then removed and dried at 100° C. in a rotary drier. The dry powder was recovered to the extent of 78 percent of the theoretical yield, based on the starting materials used, and was crushed, mixed with about 2 percent of a lubricant grade graphite and expressed into pellets about one-quarter inch in diameter and one-quarter inch long. The graphite was burned off by treating with air and steam at about 650° C. for about 6 hours. The resulting catalyst pellets were tested as dehydrogenation and cracking catalyst at 700° C., 150 v./v./hr. (volumes of gas per unit volume of catalyst per hour) (S.T.P.) of 99 percent n-butane, 1,500 v./v./hr. or 3,000 v./v./hr. of steam and 0.5 hr. of 1.0 hr. cycle, half of which was regeneration of catalyst accomplished by passing 400 or 85 v./v./hr. of air and 1,500 or 3,000 v./v./hr. of steam, respectively, at the reaction temperature. The results set forth in the following table are all based on the carbon content of the amount of butane converted.

Catalyst, chromium to nickel ratio	6/1	6/1	6/1
pH of precipitation	4.5	4.5	6.0
v./v./hr. steam	1,500	3,000	3,000
Cycle, hours	0.5	1.0	1.0
Product Data			
% Conversion	34	23	23
% Yield C_2H_4 and C_3H_6	59	61	60
% yield 1-C_4H_8	5.5	10	3.5
% Yield 2-C_4H_8	4.5		3
% Yield 1,3-C_4H_6	17.5	16	19.5

EXAMPLE 2

In a like manner employing the same catalyst, as well as one prepared in a similar manner but having a Cr/Ni ratio of 9 and feeding 99 percent butene at 650° C., 300 v./v./hr. (S.T.P.) and 6,000 v./v./hr. of steam and 1 hour cycles, there was obtained the following results:

Cr/Ni ratio	6/1	9/1
pH	4.5	4.5
Product Data		
% Conversion	17.5	13
% Yield 1,3-C_4H_6	93.5	86.5

EXAMPLES 3–5

Nickel chloride, 15 gram moles, as 22 weight percent aqueous solution thereof was mixed in a vessel with 10.3 gram moles of phosphoric acid as a 75.5 weight percent aqueous solution and the resulting mixture was diluted with water to a total volume of 65 gallons. Upon completion of the addition of the above-enumerated chemicals to the vessel reactor, 43.3 gram moles of an aqueous 13.6 weight percent ammonium hydroxide solution was slowly added while continuously stirring the reaction mass over 2.3 hours until the pH of the reaction mass remained constant. The final pH remained at a constant value of 7.8. Thereafter, the reaction mass was allowed to settle overnight after which the supernatant liquid was drawn off (approx. 60 gallons decanted) and the resulting thick slurry filtered and washed with water. The filtrate was discarded. In the specific instance, the slurry was washed by decantation with water 3 times until chloride free, then removed and dried at 100° C. in a rotary drier. The dry powder was recovered to the extent of 99 percent of the theoretical yield, based on the starting materials used, and was crushed, mixed with about 2 percent by weight of a lubricant grade graphite and expressed into pellets about one-quarter inch in diameter and one-quarter inch long. The graphite was burned off by treating the pellets with air and steam at about 650° C. for about six hours. The resulting catalyst pellets were tested as cracking or dehydrogenation catalyst with 99 percent n-butane or 99 percent butene, steam and 1.0 hour cycles. The results of such operations are set forth in the following table. All yields are based on the carbon content of the amount of hydrocarbon converted. The various catalysts were prepared in the same manner as set forth above with adjustment in the amount of ammonia only to obtain the stated pH of precipitation. Regeneration of catalyst beds was for 30 minutes duration of the 1.0-hour cycles using 680 v./v./hr. air and 6,000 v./v./hr. steam for n-butene and 85 v./v./hr. air and 3,000 v./v./hr. steam for n-butane at 1 atom pressure.

	Example No.					
	3		4		5	
	pH of precipitation, dry power					
	6.0		7.8		8.5	
Percent recovery	74		99		115	
Feedstock	C_4H_{10}	C_4H_8-1	C_4H_{10}	C_4H_8-1	C_4H_{10}	C_4H_8-1
V./v./hour (STP) feedstock	150	300	150	150	150	150.
V./v./hour (STP) steam	3,000	6,000	3,000	3,000	3,000	3,000.
Temperature ° C	700	650	700	700	700	690.
Product data; percent conversation	18.5	23	23.5	45.5	19.5	42.5.
Percent yield:						
Butene-1	7.5		7		7.5	
Butene-2	0		5.5		11	
Butadiene	24	93.5	15	87.5	19	89.5.
C_2H_4	22.5		28.5		23	
C_3H_6	25.5		27.5		25.5	

In comparison, pure $Ni_3(PO_4)_2$ made using NaOH instead of NH_4OH degraded butene-1 to CO_2 and H_2 at 6000° C. However, replacement of 10, 25 and up to 50 percent of the NH_4OH used in the foregoing examples with NaOH, results in catalyst of comparable quality to that shown in the table.

EXAMPLE 6

Nickel chloride, 21 gram moles, as an 8 weight percent aqueous solution thereof, was mixed in a vessel with 3.48 gram moles of chromium chloride as a 26.7 weight percent aqueous solution and 17.9 gram moles of phosphoric acid as a 75.5 weight percent aqueous solution and the resulting mixture is diluted with water to a total volume of 105 gallons. Upon completion of the addition of the above-enumerated chemicals to the vessel reactor, 53.8 gram moles of an aqueous 13.4 weight percent ammonium hydroxide solution was slowly added while continuously stirring the reaction mass over 2.5 hours of reaction at which time the reaction was considered complete as the pH remained constant at 5.7. Thereafter the

reaction mass was allowed to settle overnight after which the supernatant liquid was drawn off (approximately 61 gallons decanted) and the resulting thick slurry filtered and washed with water. The filtrate was discarded. In the specific instance the slurry was washed by decantation with water 13 times until chloride free, then removed and dried at 100° C. in a rotary drier. The dry powder was recovered to the extent of 57 percent of the theoretical yield, based on the starting materials used, and was crushed, mixed with about 2 percent of lubricant grade graphite, and expressed into pellets about one-quarter inch in diameter and one-quarter inch long. The graphite was burned off by treating the pellets with air and steam at about 650° C. for about 6 hours. The resulting catalyst pellets were treated in a steam atmosphere for 24 hours at 700° C. and then were tested as cracking catalyst at 650° C., 150 v./v./hr. with 99 percent n-butane, 3,000 v./v./hr. of steam and 1 hr. cycle, 50 percent of which was regeneration using 85 v./v./hr. of air and 3,000 v./v./hr. of steam at the reaction temperature. There was obtained a yield of 82 percent of C_3H_6 and 18 percent yield of CH_4 based on the carbon content of the amount of butane converted (91 percent per pass).

EXAMPLE 7

A catalyst was prepared in a similar manner to example 1 except the mole ratio of nickel to chromium was 9 to 1 and the final pH was 5.8. Seventy percent of theoretical yield was obtained as a dry powder. After being pelletized, the catalyst was employed in the test procedure outlined in example 6 to obtained a 76.3 percent conversion of butane fed and an 81 percent yield of C_3H_6 and 19 percent yield of methane.

EXAMPLES 8–11

Nickel chloride, 21 gram moles, as an 8 weight percent aqueous solution thereof was mixed in a vessel with 3.48 gram moles of chromium chloride as a 26.7 weight percent aqueous solution and 17.9 gram moles of phosphoric acid as a 75.5 weight percent aqueous solution and the resulting mixture was diluted with water to a total volume of 105 gallons. Upon completion of the addition of the above-enumerated chemicals to the vessel reactor, 91.4 gram moles of an aqueous 13.4 weight percent ammonium hydroxide solution was slowly added over 2.5 hours with continuous stirring of the reaction mass. The reaction was considered complete when the pH remained constant at 8.3. Thereafter the reaction mass was allowed to settle overnight after which the supernatant liquid was drawn off (approximately 76 gallons decanted) and the resulting thick slurry filtered and washed with water. The filtrate was discarded. In the specific instance the slurry was washed by decantation with water 12 times until chloride free, then removed and dried at 100° C. in a rotary drier. The dry powder was recovered to the extent of 93 percent of the theoretical yield, based on the starting materials used, and was crushed, mixed with 2 percent by weight of a lubricant grade graphite and expressed into pellets about one-quarter inch in diameter and one-quarter inch long. The graphite was burned off by treating the pellets with air and steam at about 650° C. for about 6 hours. The resulting catalyst pellets were tested as cracking and dehydrogenation catalyst at the temperature, feed name, and at the feed rates set forth below. All yields are based on the carbon content of the amount of hydrocarbon converted.

	Example Number			
	8	9	10	11
Feed	C_4H_{10}	C_4H_{10} [1]	99% [1] C_4H_8	92% [1] C_3H_6
V./v./hour feed	150	150	300	300
V./v./hour steam	3,000	3,000	6,000	6,000
Temperature, ° C.	640	700	650	800
Cycle time, hour [2]	0.5	1.0	1.0	1.0
Product; percent conversion	19	24	22	80
Percent yield:				
$C_2H_4+C_3H_6$	10	54.5		
C_4H_8-1	21.5	28.5		
C_4H_8-2	25			
1,3-C_4H_6	38		95.5	2.5
C_2H_4				35
C_2H_2				7
C_3H_4				8.5

[1] Catalyst was prepared with nickel to chromium ratio of 9 to 1, and otherwise catalytic preparation the same as set forth.

[2] Half cycle time with both hydrocarbon and steam followed by half time on steam and air. Regeneration air was 400 v/v/hr. for C_4H_{10} runs and 680 v/v/hr. for other two.

1. Catalyst was prepared with nickel to chromium ratio of 9 to 1, and otherwise catalytic preparation the same as set forth.
2. Half cycle time with both hydrocarbon and steam followed by half time on steam and air. Regeneration air was 400 v./v./hr. for C_4H_{10} runs and 680 for other two.

The following examples illustrate the present invention when it is applied to converting propylene to more valuable products.

EXAMPLE 12

A coprecipitated nickel-chromium phosphate prepared in the manner of copending application Ser. No. 335,810, having about 9 moles of nickel per mole of chromium, pelletized to three-sixteenths inch diameter pellets, three-sixteenths inch long, was employed. A 1-inch ID, 24-inch long cylindrical glass tube reactor was loaded in its central portion for about 1 foot with about 150 cc. of catalyst pellets. The space on each end was filled with Raschig rings. The tube was heated by external electric heating tape wrapped about the exterior. About 300 volumes of propylene-rich feed per volume of catalyst per hour was mixed with 6,000 volumes of steam per volume of catalyst per hour and introduced into the reactor. The gases issuing from the reactor were analyzed and found to have the following distribution:

	Mole percent			
		Product		
Exit gas	Feed	775°	800°	815°
Increase over feed		131	174	342
Propylene (C_3H_6)	93	23.8	11.2	1.7
Propadiene ($H_2C=C=CH_2$)	1.3	2.0	1.4	0.4
Propyne ($HC\equiv C-CH_3$)	1.4	4.3	3.4	1.1
Propane (C_3H_8)	4.3			
Butadiene (C_4H_6)	0	1.4	1.0	0.3
Methane (CH_4)	0	33.5	44.0	61.6
Ethylene (C_2H_4)	0	26.8	28.1	21.3
Acetylene (C_2H_2)	0	4.4	5.8	5.0
Balance		(1)	(1)	(1)
Conversion of propylene		62.2	79.5	96.0
Yields C_3H_4's		6.7	5.4	0.6
Yields products [2]		32.0	49.5	42.7
Selectivity to products [2]		51.5	62.2	44.5

[1] Balance—low molecular weight byproducts, propane, butane, butene, as well as CO_2.

[2] Propadiene, propyne, butadiene, ethylene, acetylene.

EXAMPLE 13

In the manner of Example 1 employing the same feed rates, ratios and catalytic volumes and a coprecipitated phosphate catalyst prepared in the manner of application, Ser. No. 335,784, having about 6 moles of chromium per mole of nickel and pelletized into three-sixteenths inch diameter, three-sixteenths inch long pellets, a propylene-rich stream was dehydrogenated. The results are set forth in the following table:

	Mole percent			
		Product		
Exit gas	Feed	805°	825°	875°
Increase over feed		71.5	90.5	155
Propylene (C_3H_6)	93	41.2	28.3	3.6
Propadiene ($H_2C=C=CH_2$)	1.3	2.1	2.2	0.9
Propyne ($HC\equiv C-CH_3$)	1.4	4.3	5.0	2.1
Propane (C_3H_8)	4.3			
Butadiene (C_4H_6)	0	1.6	1.9	0.6
Methane (CH_4)	0	26.6	28.1	45.0
Ethylene (C_2H_4)	0	16.8	24.6	30.3
Acetylene (C_2H_2)	0	2.8	5.0	10.4
Conversion of propylene		42.4	57.2	92.8
Yields C_3H_4's		5.5	7.4	2.6
Yields products		26.8	41.1	58.7
Selectivity to products		63.2	71.8	63.2

In order to show that the activity was that of the catalyst, blank runs using Raschig rings were made at 804° C. and 875° C. The results are set forth in the table below:

Exit gas	Mole percent		
		Product	
	Feed	804°	875°
Increase over feed		6.5	37.5
Propylene (C_3H_6)	92.9	87.2	37.8
Propadiene ($H_2C=C=CH_2$)	1.3	1.3	1.9
Propyne ($HC\equiv C-CH_3$)	0	(1)	(1)
Propane (C_3H_8)	0		
Butadiene (C_4H_6)	1.4	0.5	2.6
Methane (CH_4)		2.7	23.2
Ethylene (C_2H_4)		4.3	32.4
Acetylene (C_2H_2)			0.1
Conversion		4.3	46.8
Yield C_3H_4's		(−1.5)	(−0.3)
Products, yield		2.4	36.4
Selectivity to products		55.0	77.8

[1] Included in butadiene analysis mole percent if present.

EXAMPLE 14

Employing 92 percent propylene and steam at the same rate as butene and steam and the 6/1 Cr/Ni catalyst used in example 2 above, at 825° C., there was obtained a 57 percent conversion of propylene fed. The yield of desirable products based on propylene consumed was 42 percent ethylene, 18.5 percent propadiene, 8.5 percent acetylene and 6.5 percent butadiene.

We claim:

1. The method which comprises dehydrogenating and/or cracking an aliphatic hydrocarbon having at least three carbon atoms by passing the hydrocarbon together with steam at a temperature between 600° and 750° C. in contact with a catalyst consisting of a nickel phosphate prepared by mixing a solution of soluble salt of nickel with a soluble source of orthophosphate ion and precipitating in the gel form nickel phosphate at a pH of between about 4 to 9, established at least in part by the presence of ammonium hydroxide.

2. The method of claim 1 which comprises passing hydrocarbon vapors containing a paraffin having four carbon atoms and between 10 and 20 volumes per volume of hydrocarbon of steam into contact with the catalyst.

3. A process for dehydrogenating propylene to ethylene, propyne and propadiene which comprises passing gaseous propylene at a temperature of about 700° to 1,000° C. over a chromium-nickel-containing coprecipitated phosphate catalyst and in the presence of steam, said propylene being employed in proportions to provide space velocities of from about 100 to 500 volumes of propylene per volume of catalyst per hour at standard temperature and pressure and from about 10 to about 30 volumes of steam per volume of propylene feed, said catalyst containing from about 6 to 9 moles of chromium per mole of nickel or 6 to 9 moles of nickel per mole of chromium, and coprecipitation in the gel form at a pH of between about 4 to 9 established at least in part by the presence of ammonium hydroxide.

4. The process of claim 3 wherein said catalyst is a phosphate containing from about 6 to 9 moles of chromium per mole of nickel.

5. The process of claim 4, wherein said temperature is from about 805° C. to about 875° C. and said chromium to nickel ratio is 6 to 1 respectively.

6. The process of claim 3 wherein said catalyst is a phosphate containing 6 to 9 moles of nickel per mole of chromium.

7. In the process of claim 6, 815°said temperature is from about 755° to about 815° C. and said nickel to chromium ratio is 9 to 1 respectively.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,621,071 Dated November 16, 1971

Inventor(s) Charles R. Noddings, Andrew J. Dietzler, Ronald G. G

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 35, change "setting" to read -- settling --.

Column 3, line 15, after "phosphate" insert -- precipitated --.

Column 6, line 34, change "atom" to -- atm. --.

line 57, change "6000°C." to read -- 600°C. --.

Column 7, line 30, change "obtained" to read -- obtain --.

Column 8, lines 8, 9, 10, 11, 12, 13, delete

1. Catalyst was prepared with nickel to chromium ratio of 9 to 1, and otherwise catalytic preparation the same as set forth.

2. Half cycle time with both hydrocarbon and stream followed by half time on steam and air. Regeneration air was 400 v./v./hr. for C_4H_{10} runs and 680 for other two.

Column 10, Claim 7, line 32, delete "815°".

line 32, before "said" insert -- wherein --.

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents