

Nov. 10, 1953

W. H. LANG ET AL
AROMATIZATION REFORMING AND CATALYSTS
FOR EFFECTING THE SAME

2,658,858

Filed June 22, 1949

2 Sheets-Sheet 1

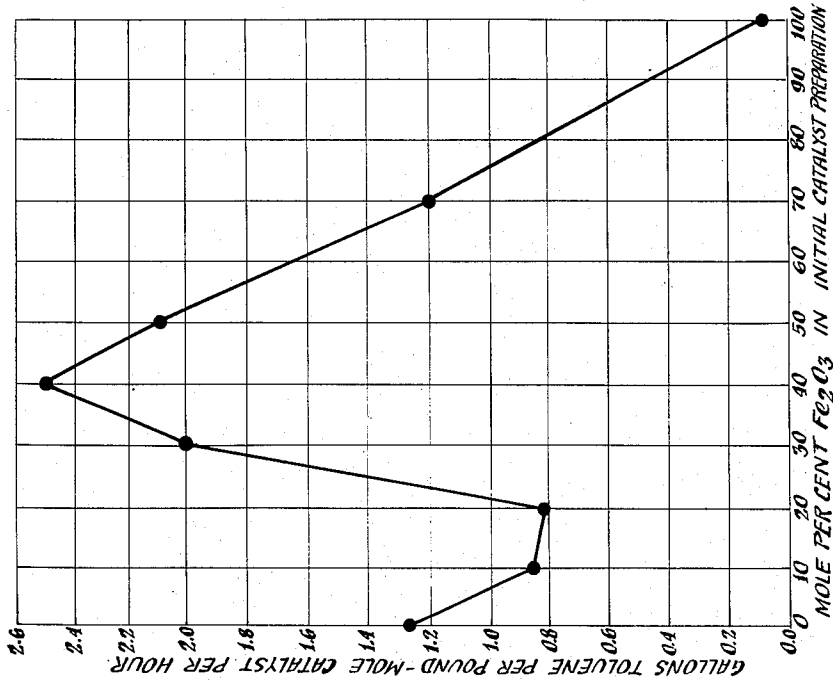


Fig. 1

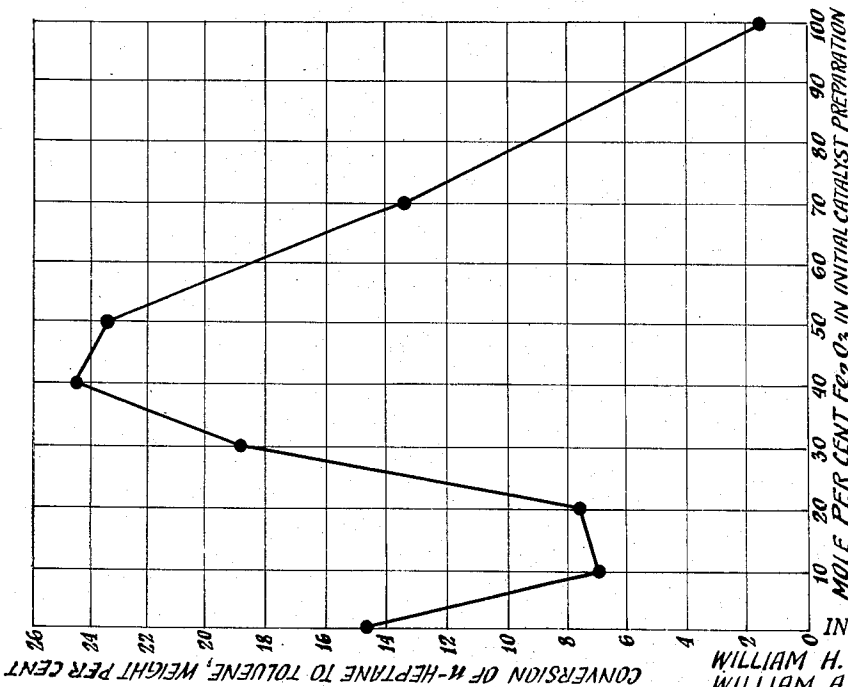


Fig. 2

INVENTORS
WILLIAM H. LANG
WILLIAM A. STOVER
CARLOS L. GUTZEIT

BY *James H. [Signature]*
ATTORNEY

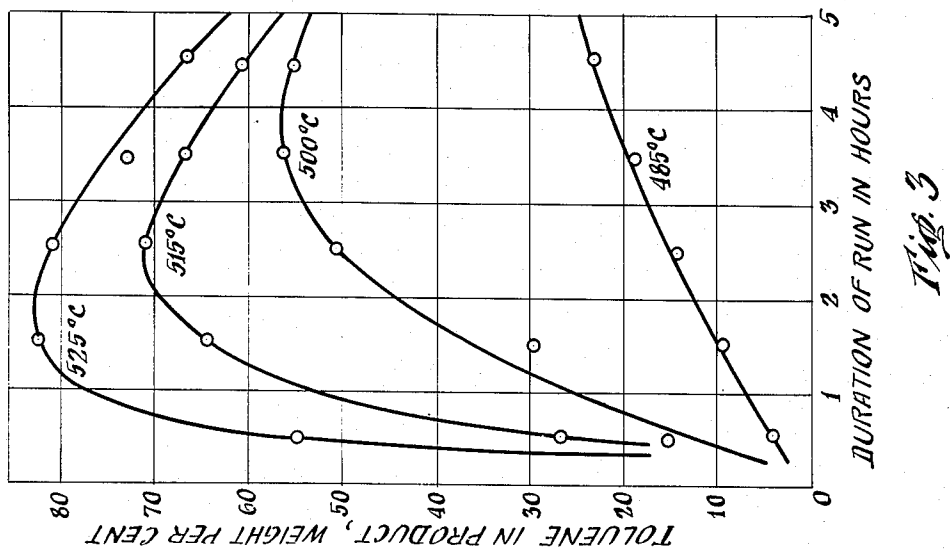
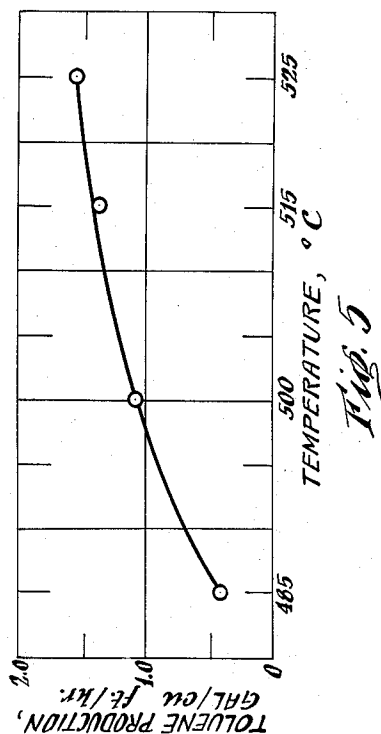
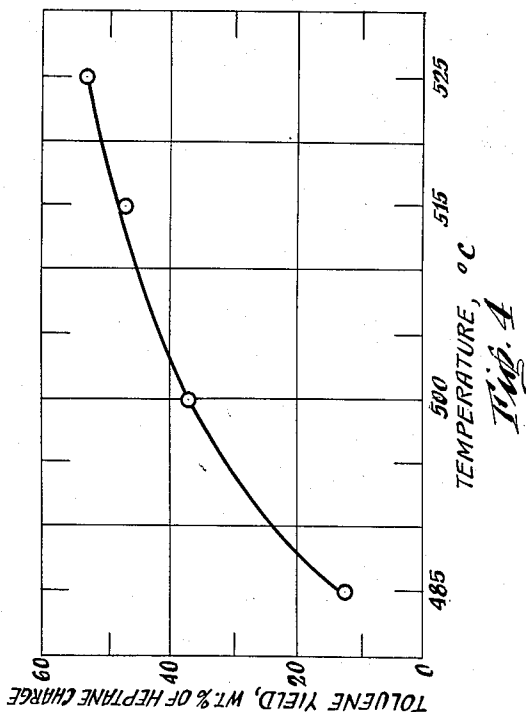
Nov. 10, 1953

W. H. LANG ET AL.
AROMATIZATION REFORMING AND CATALYSTS
FOR EFFECTING THE SAME

2,658,858

Filed June 22, 1949

2 Sheets-Sheet 2



INVENTORS
WILLIAM H. LANG
WILLIAM A. STOVER
CARLOS L. GUTZEIT
BY *Jay R. Gindie*
ATTORNEY

UNITED STATES PATENT OFFICE

2,658,858

AROMATIZATION REFORMING AND CATALYSTS FOR EFFECTING THE SAME

William H. Lang, William A. Stover, and Carlos L. Gutzeit, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

Application June 22, 1949, Serial No. 100,562

4 Claims. (Cl. 196—50)

1

This invention relates to new catalysts containing chromium oxide and oxides of metals of the iron group, and to a process for effecting the aromatization of aromatizable hydrocarbons. It is more particularly concerned with new catalysts of the type referred to prepared under conditions adapted to form mixed oxides which have a specific activity for the dehydrocyclization of normal paraffins.

Aromatization is a term well known in the art and connotes the selective conversion of paraffinic, olefinic or naphthenic hydrocarbons, containing at least six carbon atoms per molecule, generally referred to as aromatizable hydrocarbons, into aromatic hydrocarbons having the same number of carbon atoms per molecule. The formation of aromatic hydrocarbons by condensation of monoolefinic, diolefinic or acetylenic hydrocarbons, through homopolymerization or copolymerization, is not included within the accepted meaning of the term. Aromatization may involve one reaction or two separate and distinct reactions, depending upon the nature of the aromatizable hydrocarbon which is subjected to the treatment. When aromatizable paraffinic or olefinic hydrocarbons are the hydrocarbons to be aromatized, the reactions which must occur to produce an aromatic ring are dehydrogenation and cyclization. These reactions are collectively referred to, in the art, as dehydrocyclization. On the other hand, when aromatizable alicyclic hydrocarbons are the hydrocarbons to be aromatized, dehydrogenation is the only reaction that must take place.

As is well known to those familiar with the art, unsaturated hydrocarbons, as a class, possess octane number ratings that are higher than those of the corresponding saturated hydrocarbons, and aromatic hydrocarbons, as a class, possess octane number ratings that are higher than those of aliphatic and naphthenic or alicyclic hydrocarbons, saturated and unsaturated, although the octane number ratings of certain individual aliphatic hydrocarbons are as high or even higher. Therefore, aromatization is an expedient whereby the aromatizable low-octane aliphatic or alicyclic hydrocarbons can be converted into the corresponding but higher-octane aromatic hydrocarbons. Aromatization, of course, is not only applicable to the treatment of individual aromatizable hydrocarbons, but also, to the treatment of mixtures of aromatizable hydrocarbons. Such operations are referred to as aromatization reforming, and the conditions of temperature, pressure, and residence time are referred to as aromatization reforming conditions.

The hydrocarbon mixtures which are subjected to aromatization reforming may contain, and generally do contain, non-aromatizable hydro-

2

carbon constituents. Typical of these hydrocarbon mixtures are petroleum naphthas. As a result of the aromatization reforming operation, the aromatizable hydrocarbon components of the mixtures are converted into the corresponding but ordinarily higher-octane aromatic hydrocarbons, while the non-aromatizable hydrocarbon components are dehydrogenated to the corresponding higher-octane unsaturated hydrocarbons, as stated hereinbefore. In view of the ever-increasing demand for higher-octane fuels, the utility and advantages of a commercially feasible process for effecting aromatization reforming are manifest.

Accordingly, several aromatization reforming processes have been proposed. Thus, it has been suggested to treat petroleum oils, under aromatization reforming conditions, in the presence of catalysts containing iron oxide or chromium oxide as the active constituent. In the processes utilizing catalysts containing chromium oxide as an active constituent, the catalyst-poisoning effect of traces of iron has been recognized and this has led to the proposal of numerous methods to prevent the contamination of such catalysts by iron. These methods include the use of non-ferrous metals as liners for reactors and sulfur-poisoning of ferrous metals to avoid migration of iron from the reactor walls to the catalyst.

In catalytic hydrogenation and dehydrogenation processes, chromites of metals of the iron group, i. e., iron, nickel and cobalt, such as $\text{Fe}(\text{CrO}_2)_2$, are milder catalysts than chromium oxide or the metals of the iron group per se from which these chromites may be considered to be derived. This milder catalytic action is exemplified by the formation of methanol and other oxygen organic compounds obtained when carbon monoxide and hydrogen are allowed to react in the presence of these chromite catalysts. When carbon monoxide and hydrogen are allowed to react in the presence of a metal of the iron group per se, under the same reaction conditions, methane, rather than methanol, is produced. The milder catalytic activity of these chromites has led to their use in the selective desulfurization of sulfur-containing petroleum oils under hydrogen pressure and as catalysts in aromatization reforming operations. Thus, for example, U. S. Patent Nos. 2,315,144; 2,325,034; 2,393,288; 2,398,919 and 2,409,587 disclose processes for effecting reforming and desulfurization of hydrocarbon fractions through the use of molybdates and chromites of metals of the iron group as catalysts. The latter are prepared by precipitation of normal salts of molybdic or chromic acid by a simple metathetical reaction. This limits the composition of the catalytically active materials to ratios of molybdenum or chromium to iron group metal which will react in aqueous

solution to form insoluble products of fixed composition.

The definition of metal chromite catalysts is controversial. It is based normally upon the method of preparing mildly active hydrogenation catalysts effective in the production of oxygen-containing compounds, such as alcohols, as described in U. S. Patent Nos. 1,746,782 and 1,746,783. The preparation involves the exothermic decomposition of water-insoluble, precipitated double salts of hexavalent chromium and a hydrogenating metal which may be an iron group metal. The preparation of such catalysts has been discussed in detail by Calingaert and Edgar, *Ind. Eng. Chem.*, 26, 878 (1934) and by Adkins in "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," *The University of Wisconsin Press* (1937). It should be noted, however, that catalysts equal in activity to those described in U. S. Patent Nos. 1,746,782 and 1,746,783, have been obtained by precipitation of mixed copper and chromium salts with ammonium carbonate [see Conner, Folkers and Adkins, *J. Am. Chem. Soc.*, 53, 2012 (1931)]. It should be noted also that while the method of chromite formation set forth in these two patents is satisfactory for the preparation of copper or zinc chromites, which are those usually prepared by this method; it is difficult to prepare iron chromite in this manner.

While the nature of chromite catalysts such as copper chromite is the subject of controversy, the chromites are recognized by crystallographers as a type of spinel and are defined by their composition and crystal arrangement [see Wyckoff, "The Structure of Crystals," *The Chemical Catalog Co.* (1931 et seq.)]. There is no literature relating catalytic activity to structure of well-crystallized spinels.

Suitably combined, intimate mixtures of iron oxide and chromium oxide, prepared in a manner to avoid chromite formation, have been disclosed as dehydrogenation catalysts to effect the dehydrogenation of butylenes to butadiene in a continuous operation. For instance, in U. S. Patent No. 2,408,140, it has been proposed to prepare a catalyst effective in the dehydrogenation of butylenes to butadiene by calcining a mixture of pigment-grade iron oxide, commercial chromic oxide and a potassium salt. Mechanical mixtures of these metal oxides, prepared from them in the dry state, however, are not effective as catalysts in aromatization reforming. For example, a catalyst thus prepared will not catalyze the aromatization of n-heptane, a hydrocarbon which is generally used in the evaluation of aromatization reforming catalysts.

It has now been discovered that it is possible to effect the aromatization of aromatizable hydrocarbons and to carry out aromatization reforming of hydrocarbon mixtures containing aromatizable hydrocarbons in the presence of mixtures of chromium oxide with oxides of metals of the iron group. As stated hereinbefore, aromatization catalysts, the active constituent of which is chromium oxide, are fairly active catalysts and appreciably more effective, as aromatization catalysts, than catalysts the active constituent of which is iron oxide. However, it has now been found that when iron oxide is mixed with specified amounts of chromium oxide, in the hydrated oxide state and under conditions to avoid chromite formation, the aromatization activity of the mixtures is greater than either constituent alone. Also, it has been found that the mixtures of metal

oxides which are effective as aromatization reforming catalysts herein, are also effective as desulfurization catalysts.

Accordingly, it is an object of the present invention to provide a novel and efficient aromatization and aromatization reforming process. Another object is to provide an efficient and commercially feasible catalytic aromatization reforming process. A further object is to provide a novel catalytic aromatization reforming process utilizing certain mixtures of chromium oxide with iron oxide, as a catalyst. A specific object is to provide new catalysts containing chromium oxide and oxides of metals of the iron group. An important object is to provide a process for producing new catalysts containing chromium oxide and oxides of metals of the iron group.

Other objects and advantages of the present invention will become obvious to those skilled in the art from the following description taken in conjunction with the drawings, in which:

Figure 1 shows two curves representing graphically the relationship between the conversion of n-heptane into toluene, under aromatization reaction conditions, and in the presence of the catalysts contemplated herein, and the concentration of iron oxide in the catalysts;

Figure 2 shows two curves representing graphically the relationship between the ratio of toluene to catalyst per hour in the conversion of n-heptane to toluene, under aromatization reaction conditions and in the presence of the catalysts contemplated herein, and the concentration of iron oxide in the catalysts;

Figure 3 shows a series of curves indicating graphically the effect of temperature and duration of run on the dehydrocyclization of n-heptane with the catalysts of the present invention;

Figure 4 shows a curve indicating graphically the effect of temperature on the conversion of n-heptane to toluene in accordance with the present invention; and

Figure 5 shows a curve indicating graphically the effect of temperature on the rate of toluene formation from n-heptane, in accordance with the present invention.

Broadly stated, the present invention provides:

1. A catalyst comprising intimate mixtures of chromium oxide with specified amounts of oxides of metals of the iron group, prepared from the moist, undried hydrous oxides, calcined at specified temperatures and under conditions to prevent chromite formation;

2. A process for desulfurizing sulfur-bearing hydrocarbon fractions, which comprises contacting a sulfur-bearing hydrocarbon fraction, in the presence of hydrogen, under aromatization reforming conditions, with one of the aforesaid catalysts; and

3. A process for effecting the aromatization of aromatizable hydrocarbons or the aromatization reforming of hydrocarbon mixtures containing aromatizable hydrocarbons, which comprises contacting said hydrocarbons, under aromatization reforming conditions, with one of the aforesaid catalysts.

In accordance with the present invention, the aromatization, aromatization reforming and desulfurization catalysts to be employed herein are intimate mixtures of an oxide or oxides of metals of the iron group with a chromium oxide. It is appreciated that these metal oxides exhibit varying states of oxidation. Thus, the term oxide of a metal of the iron group embraces ferrous oxide (FeO), ferrosferic oxide (Fe_3O_4), ferric

oxide or iron sesquioxide (Fe_2O_3), nickelous oxide (NiO), nickelous-nickelic oxide (Ni_3O_4), nickelic oxide or nickel sesquioxide (Ni_2O_3), cobaltous oxide (CoO), cobaltous-cobaltic oxide (Co_3O_4), and cobaltic oxide or cobalt sesquioxide (Co_2O_3). Similarly, the term chromium oxide embraces chromous oxide (CrO), chromium dioxide (CrO_2), chromium trioxide (CrO_3), and chromic oxide or chromium sesquioxide (Cr_2O_3). It is suspected that the state of oxidation of the oxides of the metals of the iron groups and of the chromium oxide during the reaction are somewhat critical. The exact states of oxidation during the reaction, however, are very difficult to determine and are not known at present. Nevertheless, whatever these states may be, the successful accomplishment of the desired conversions in accordance with this invention, would seem to indicate that these states are achieved and maintained under the reaction conditions of the process contemplated herein, independently of the states of oxidation of the metals in the starting catalyst. Accordingly, and in the interest of brevity, the various oxides of the metals of the iron group and the various chromium oxides will be referred to hereinafter and in the claims, as iron group metal oxides and chromium oxide, respectively, it being clearly understood that when reference is made thereto, one or more of these iron group metal oxides or chromium oxides will be intended.

While it is not possible to specify the active states of oxidation of the component metal oxides during reaction, it is possible to do so for the metal oxides in the initial catalyst preparations contemplated herein. It has been found that the state of oxidation in the initial catalyst preparations must be such as to effect miscibility of the metal oxides in all proportions, i. e., form solid solutions in all proportions. The solid solution formation may occur during the initial heat treatment.

In accordance with the rule established by Passerini [Gazz. chim. ital., 62, 85 (1932)] concerning solid solution formation between isomorphous metal oxides in which the metals have the same valence, iron oxide, for example, and chromium oxide form solid solutions in all proportions only if they correspond to alpha-ferric oxide and ordinary chromic oxide, respectively. Both these oxides crystallize as rhombohedral crystals which are isomorphous. The rule established by Passerini states:

(a) The metal oxides are miscible in all proportions if the ionic radii of the metals do not differ by more than 12 per cent;

(b) The metal oxides are partially miscible if the ionic radii of the metals differ by more than 12 per cent but less than 30 per cent. In such cases, there are two regions of miscibility (one stable phase) separated by a miscibility gap representing two stable phases of solid solutions each of which corresponds to a limiting solubility concentration;

(c) Solid solution does not occur if the ionic radii of the metals differ by more than 30 per cent.

Accordingly, the active metal oxides in the initial catalyst preparations of the present invention correspond to subdivision (a) of the rule, while the initial states of oxidation of the coprecipitated chromic oxide-alumina catalysts of U. S. Patent Nos. 2,249,337; 2,258,111; and 2,363,498 and of the coprecipitated ferric oxide-

alumina catalysts of U. S. Patent No. 2,449,295 correspond to subdivision (b) of the rule.

As stated hereinbefore, chromium oxide or iron oxide, per se, possess aromatization catalytic action. However, and also as stated hereinbefore, the avoidance of contamination of chromium oxide aromatization catalysts by iron is well established. Thus, for example, the presence of iron oxide in chromium oxide catalysts, otherwise prepared in accordance with the present invention, in amounts of up to about 20 mol per cent, in terms of the sesquioxides (Fe_2O_3 and Cr_2O_3), appreciably reduces the aromatization catalytic activity of the chromium oxide. However, larger amounts appreciably increase the aromatization catalytic activity of the chromium oxide. On the other hand, when the amounts are in excess of 65 mol per cent, in terms of the sesquioxides, the aromatization catalytic activity of the chromium oxide is again materially reduced. Because of these facts, the ratio of iron group metal oxides to chromium oxide, in the catalysts to be used in the process of this invention, is very critical. This is illustrated in Figures 1 and 2 of the drawings. The data for these curves were obtained as set forth in Example 1, described hereinafter.

It will be noted that the addition of relatively small amounts of iron oxide to chromium oxide produces a decrease in catalytic activity. This is in complete accord with the prior art. However, at higher concentrations of iron oxide in the iron oxide-chromium oxide mixtures, within the range of mol per cent ratios corresponding to $\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3$ —about 30:70 to about 70:30, the iron oxide-chromium oxide mixtures are equal or superior to either chromium oxide or iron oxide.

Therefore, with respect to composition of the catalytically active metal oxides, the catalysts of the present invention may be defined as intimate mixtures of chromium oxide with iron group metal oxides in which the mol per cent ratios, expressed on the basis of the metal sesquioxides, are $\text{Cr}_2\text{O}_3:\text{M}_2\text{O}_3$ between about 35:65 and about 70:30, wherein M represents the iron group metal or metals. The preferred compositions correspond to mol per cent ratios of $\text{Cr}_2\text{O}_3:\text{M}_2\text{O}_3$ between about 40:60 and about 70:30. It must be clearly understood that the expression of the mol ratios in terms of the metal sesquioxides is only a convenient way for indicating substitution of atomic equivalents of one metal for another and does not necessarily represent the catalytically active forms of the metal oxides.

The catalytically active iron group metal oxide-chromium oxide mixtures to be used herein may be produced by any of the well known methods utilized in the preparation of active metal oxide mixtures from the hydrous oxides, such as by coprecipitation, cogelation or separate precipitation and wet mixing of the hydrous oxides, or, in general, by any method providing an intimate contact between the hydrous oxides of iron group metal and chromium, collectively referred to herein as intimate mixtures of the metal oxides prepared from the moist, undried hydrous oxides. In accordance with the present invention, it is essential that the catalysts be prepared from hydrous oxides. Accordingly, the catalysts contemplated herein are prepared, as is well known in the art, by:

(a) Coprecipitation of hydrous oxides or of other compounds which decompose to form solely an intimate mixture of active metal oxides under conditions of calcination; or

(b) Coprecipitation of hydrous oxides or of

other compounds under conditions of calcination to form solely metal oxides, these metal oxides comprising the catalytically active metal oxides as well as substantially inert, refractory metal oxides which serve as spacers for the active metal oxide particles, thereby decreasing sintering or crystallization; or

(c) Impregnation of substantially inert, refractory metal oxide supports with true aqueous solutions, such solutions being selected to avoid hydrolysis or other decomposition during the impregnation step but which decompose under conditions of calcination to leave a residue which consists solely of an intimate mixture of the catalytically active metal oxides.

Typical of the compounds from which the catalysts may be prepared are the water-soluble metal salts the anions of which are decomposed by heat and oxidation, for example, the iron, nickel, cobalt or chromium nitrates or acetates. Sulfates may be used also except when a two-step precipitation is employed in which a sol is initially produced at a pH value of below 7. A small amount of sulfate ions on the catalyst surface, such as that which remains after rapid precipitation at a pH value above 7 or by washing the hydrated oxides precipitated from nitrates or acetates with ammonium sulfate, is highly desirable because it decreases coke deposition on the catalyst during utilization in the aromatization or aromatization reforming or desulfurization process. Nonvolatile anions such as chlorides are preferably absent. Precipitation may be effected by ammonium, potassium or sodium hydroxides and/or their carbonates. The hydroxides can be used to effect either slow or rapid precipitation of the iron group metal and/or chromium hydroxides. The carbonates may be employed only when rapid precipitation is desired. It will be noted from the foregoing that the catalysts of the present invention differ from those described in U. S. Patent Nos. 2,315,144; 2,325,034; 2,393,288; 2,398,919 and 2,409,587 in that the conditions involved in their preparation preclude the formation of normal salts between the catalytically active components of the catalysts and also avoid the formation of well-defined crystals between the catalytically active metal oxides.

Whether the hydrous oxides or metal hydroxides have been coprecipitated or cogelled or precipitated separately and then mixed while wet, these materials are subsequently dehydrated by, for example, heating at a suitable temperature [about 70° C. (160° F.) to about 110° C. (230° F.)] to produce the corresponding mixtures of iron group metal and chromium oxides. The resulting mass is subsequently comminuted and then calcined at temperatures falling within the range varying between about 350° C. (662° F.) and about 600° C. (1112° F.) and, preferably, between about 500° C. (932° F.) and about 600° C. (1112° F.), for about 5 to about 10 hours, under conditions such that chromite formation does not occur, i. e., under conditions such that the chromium is not oxidized to the hexavalent form. Such calcination, as is well known in the art, is effected in a current of hydrogen, carbon dioxide, steam, nitrogen, or mixtures thereof. It may be carried out in a current of air or oxygen-containing gases provided that the catalysts contain organic materials such as starch or organic lubricants for pelleting, such as stearin.

In view of the foregoing, it will be noted that the catalysts contemplated herein are different

from those described in U. S. Patent No. 2,408,140 in at least one very important respect, viz., the temperature of calcination. While high temperature calcination does not lead to chromite formation, it nevertheless causes recrystallization [see Milligan and Merten, *J. Phys. and Colloid Chem.*, 51, 521 (1947)]. The deleterious effect of high temperature calcination on the dehydrocyclization activity of the catalysts of the present invention is illustrated by Example 2 set forth hereinafter.

The catalytically active mixtures of iron group metal oxides with chromium oxide may be used alone or in conjunction with substantially inert, from a dehydrocyclization catalytic activity standpoint, refractory oxides such as alumina, beryllia, titania or zirconia. These materials serve as spacers for the catalytically active oxides and, also, as stabilizers against crystallization and loss of structure. Silica is preferably absent because it tends to decrease the selectivity of the catalysts contemplated herein, although small amounts, the cracking action of which has been suppressed, such as that which occurs in calcined bauxite, may be employed.

These refractory oxides may constitute a major or a minor proportion of the catalyst. The amounts of refractory oxides used are not critical and, ordinarily, depend upon the iron group metal oxide present in the catalyst and upon the manner in which the catalyst is prepared. For example, when the catalysts are prepared by coprecipitation, the substantially inert refractory oxides may comprise from about 30 to about 70 mol per cent of the total oxides in the catalyst. It has been found that the preferred concentration of the refractory metal oxide increases in the order iron oxide-chromium oxide, cobalt oxide-chromium oxide, nickel oxide-chromium oxide as the active components, in the order given. The preferred amount for the iron oxide-containing catalysts is about 30 to about 50 mol per cent; the preferred amount for the nickel oxide-containing catalysts is about 50 to about 70 mol per cent. On the other hand, when the catalysts are prepared by impregnation, the refractory metal oxide support may comprise from about 80 to about 95 mol per cent of the total mixed oxides, and, preferably, from about 85 to about 95 mol per cent. Accordingly, in this specification and in the claims the expression "consisting essentially of" is not to be construed as excluding such substantially inert refractory oxides which do not affect the catalytic properties of the catalysts of the present invention.

The desirability of incorporating a substantially inert refractory metal oxide in the catalysts to prevent sintering, illustrated by examples set forth hereinafter, is substantiated by Milligan and Merten, *J. Phys. and Colloid Chem.* 51, 521 (1947). These authors have shown that ferric oxide-chromic oxide mixtures tend to crystallize at 400° C. or higher. While the catalytically active materials of this invention probably do not correspond to simple mixtures of ferric oxide and chromic oxide, it is probable that certain stages of oxidation and reduction associated with catalyst regeneration by oxidation correspond to such relatively unstable ferric oxide-chromic oxide mixtures.

The supported catalytic mixtures of the present invention are prepared in accordance with any of the well known procedures. For example, the hydrous oxides from which the catalytically active oxides are obtained may be precipitated

in the presence of the support or supports or the latter may be impregnated with salts of the metals which, upon calcination, decompose to form the catalytically active metal oxides. The catalyst supports may also be incorporated by coprecipitation, cogelation or separate precipitation and wet mixing with the active metal oxides, as is well understood in the art.

The catalysts may also contain promoters to control and to stabilize the catalytic activity of the iron group metal oxide-chromium oxide mixture. Suitable promoters are the oxides of potassium, sodium, rubidium, cesium, copper, silver, gold, calcium, strontium or barium, or compounds of these metals which yield the corresponding oxides upon calcination, such as the nitrates, acetates and sulfates. The amount of promoter should be at least about 0.2 per cent by weight, in terms of the oxide, and, preferably, is somewhat higher, for example, between about 0.5 per cent and about 5 per cent by weight. If desired, a mixture of two or more promoters may be utilized.

The promoter may be incorporated in the catalyst in accordance with any of the well established methods known in the art. For example, the hydrous oxides from which the catalytically active oxides are obtained may be precipitated in the presence of salts of the metals which yield the metal oxide promoters, or the catalyst supports may be impregnated with salts of the metals which, upon calcination, decompose to form the catalytically active metal oxides and promoters. The promoters may also be incorporated by coprecipitation, cogelation or separate precipitation and wet mixing with the catalytically active metal oxides.

The catalysts may be used in any of the conventional forms such as powder, pills, spheres, extrudates or irregular fragments, all of a size adapted for the reaction system to be employed. The catalysts may be used in onstream periods of 30 minutes to 5 hours or more, depending upon the reaction conditions of the process.

In operation, the catalysts become fouled with carbonaceous material which ultimately affects their catalytic activity. Accordingly, when the efficiency of the catalyst declines to a point where further operation becomes uneconomical, or disadvantageous from a practical standpoint, the catalyst may be regenerated, as is well known in the art, by subjecting the same to a careful oxidation treatment, for example, by passing a stream of air, oxygen, steam, or mixtures thereof over the catalyst under appropriate temperature conditions and for a suitable period of time, such as the same period of time as that of the catalytic operation. Preferably, the oxidation treatment is followed by a purging treatment, such as passing over the catalyst a stream of purge gas, for example, nitrogen, carbon dioxide, or the like.

Any aromatizable hydrocarbon or mixture of aromatizable hydrocarbons is suitable as the hydrocarbon reactant in the process of this invention. The hydrocarbon mixture may contain non-aromatizable hydrocarbons. Sources of these hydrocarbon feed stocks are petroleum naphthas, particularly those having a boiling range of from about 70° C. to about 230° C. (125-450° F.).

The reaction or contact time, that is, the period of time during which a unit volume of the reactants is in contact with a unit volume of catalyst, may vary between a fraction of a second and several minutes. Thus, the apparent

contact time may be as low as 10 seconds and as high as 20 minutes. It must be realized that these figures are at best estimates based on a number of assumptions. For all practical purposes, as in catalytic processes of the type of the present invention, the more reliable data on contact time is best expressed, as is well known in the art, in terms of liquid hourly space velocities (L. H. S. V.), in the present instance, the volume of liquid hydrocarbon reactant per volume of catalyst per hour. For example, at atmospheric pressure, it has been found that the space velocities may be varied considerably and that velocities varying between about 0.2 and about 2.5 are quite satisfactory for the purposes of the present invention.

In general, the temperatures to be used in this process vary between about 450° C. (840° F.) and about 650° C. (1200° F.) and the hydrocarbon vapor pressures employed are low, of the order of 30 pounds per square inch or less. These ranges of variation of the reaction conditions are inclusive of the following operations:

(a) Low pressure operation in the absence of diluents at temperatures of about 450° C. (842° F.) to about 600° C. (1112° F.), preferably about 485° C. (905° F.) to about 550° C. (1022° F.), at liquid hourly space velocities of about 0.2 to about 2.0, preferably, about 0.5 to about 1.0, and a total pressure of not over about 30 pounds per square inch gauge;

(b) Moderate pressure operation in the presence of hydrogen to effect desulfurization, as well as aromatization reforming, at temperatures of about 450° C. (842° F.) to about 600° C. (1112° F.), at liquid hourly space velocities of about 0.2 to about 2.0, at hydrocarbon partial pressures of not over about 30 pounds per square inch gauge, at total pressures of from about 0 to about 300 pounds per square inch gauge, with hydrogen to hydrocarbon mol ratios varying between about 1:1 to about 10:1. Preferred conditions are temperatures of about 485° C. (905° F.) to about 550° C. (1022° F.), liquid hourly space velocities of about 0.2 to about 0.5, total pressures of about 50 to about 150 pounds per square inch gauge, and hydrogen to hydrocarbon mol ratios varying between about 1:1 and about 5:1. The hydrogen dilution may be effected suitably by recycle of the hydrogen-rich gases from the process; and

(c) Low pressure operation in the presence of steam at temperatures of about 500° C. (932° F.) to about 650° C. (1202° F.), preferably, about 550° C. (1022° F.) to about 600° C. (1112° F.), liquid hourly space velocities of hydrocarbon charge of about 0.2 to about 2.5, preferably, about 0.5 to about 1.0, total pressures of not over about 50 pounds per square inch gauge, preferably not over about 30 pounds per square inch gauge, with the addition of steam in amounts to produce steam to hydrocarbon mol ratios varying from about 1:1 to about 1:6, preferably from about 1:2 to about 1:4.

The present process may be carried out by making use of any of the well known techniques for operating catalytic reactions in the vapor phase effectively. The reaction zone may be a chamber of any suitable type useful in contact-catalytic operations; for example, a catalyst bed contained in a shell, or a shell through which the catalyst flows concurrently, or countercurrently, with the reactants. The hydrocarbon vapors are maintained in contact with the catalyst at a predetermined elevated temperature and for a predetermined period of time, both as set forth hereinbe-

fore, and the resulting reaction mixture is passed through a condensing zone into a receiving chamber. It will be understood that when the catalyst flows concurrently, or countercurrently, with the reactants in the reaction chamber, the catalyst will be thereafter suitably separated from the reaction mixture by filtration or the like.

It will be apparent that the process may be operated as a batch or discontinuous process as by using the catalyst-bed-type reaction chamber in which the catalytic and regeneration operations alternate. With a series of such reaction chambers, it will be seen that as the catalytic operation is taking place in one or more of the reaction chambers, regeneration of the catalyst can be taking place in one or more of the other reaction chambers. Correspondingly, the process may be continuous when one or more catalyst chambers are used through which the catalyst flows in contact with the reactants. In such a continuous process, the catalyst will flow through the reaction zone in contact with the reactants and will thereafter be separated from the reaction mixture as, for example, by accumulating the catalyst on a suitable filter medium, before condensing the reaction mixture. In a continuous process, therefore, the catalyst—fresh or regenerated—and the reactants—fresh or recycled—will continuously flow through a reaction chamber.

The following detailed examples are for the purpose of illustrating the catalysts contemplated herein and to indicate the advantages and characteristics thereof, and, also, for the purpose of showing modes of carrying out the process of this invention. It must be clearly understood, however, that the invention is not to be construed as limited to the specific catalysts, manner of preparing them, and hydrocarbon reactants disclosed hereinafter or to the specific manipulations and conditions set forth in the examples. In each test, the hydrocarbon reactant was contacted with the catalyst in a conventional isothermal reactor. Analyses of liquid products were made by means of refractive index and mass spectrometry in the case of *n*-heptane conversions, and by means of standard methods for the determination of aromatic content and of octane number in the case of naphtha conversions. All gas analysis were made by mass spectrometry. Bromine numbers refer to the standard Norwood bromine number values.

EXAMPLE 1

EFFECT OF IRON OXIDE ON CHROMIUM OXIDE: CO-ACTIVATION FOR THE DEHYDROCyclIZATION OF *n*-HEPTANE

Catalyst preparation.—These catalysts were prepared by rapid precipitation of mixed metal oxide sols, using starch for the dual purpose of stabilizing the initial sol and of minimizing oxidation of the chromium during calcination of the dried products. The method is illustrated by the preparation of a catalyst initially corresponding to $\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=40:60$ (mol ratio).

A stock solution was prepared containing 0.6 mol $\text{Cr}(\text{NO}_3)_3$, 0.4 mol $\text{Fe}(\text{NO}_3)_3$ and 50 g. soluble starch per liter. For each liter of this stock solution, there was added, with vigorous stirring, one liter of a 2.4 molar solution of NH_4OH to obtain 80 per cent neutralization of the metal salts, the addition being controlled to prevent formation of a permanent precipitate. The product was a sol of mixed metal oxides stabilized by the remaining metal ions and by the starch. This sol was rapid-

ly precipitated with an approximately equal volume of 0.3 molar NH_4OH by continuous introduction of a thin stream of each solution into the upper part of a mixing chamber, the greater part of which was filled by a rapidly rotating, slotted, metal cylinder. The slurry of metal oxides so formed was allowed to flow by gravity into a glass chamber containing glass and calomel electrodes connected to a pH meter. The rates of addition of the reactant streams to the mixing chamber were adjusted to produce a slurry at a pH of 8.0 ± 0.05 , and the product which formed at this pH was collected. After aging for 24 hours, the precipitate was filtered off and water-washed until the wash water showed a negative test for nitrate ions with diphenylamine-sulfuric acid indicator. The precipitate was then dried at 100°C . to 110°C . in an air-circulation drying oven for about 18 hours, then heated slowly in a muffle furnace over an 8-hour period to 500°C . and maintained at this final temperature for 4 hours.

Catalysts containing chromium oxide alone and iron oxide alone were prepared similarly from chromic nitrate and from ferric nitrate, respectively. The remaining catalysts were prepared similarly from stock solutions containing chromic nitrate and ferric nitrate in the ratios required to give the desired ratios of metal oxides in the products. In each case the initial stock solution contained total metal nitrates equivalent to a 1.0 molar trivalent metal nitrate solution.

Catalyst evaluation.—The evaluation of these catalysts for *n*-heptane dehydrocyclization is summarized in Table I and the more important results are shown graphically in Figures 1 and 2. It will be observed that the coprecipitation of small amounts of iron oxide with the chromium oxide causes a drop in the activity for dehydrocyclization. However, incorporation of relatively large amounts of iron oxide in the catalysts results in an increase in dehydrocyclization activity such that within the range of composition, expressed as mol ratio of the sesquioxides, of $\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3$ of 30:70 to 70:30 the dehydrocyclization activity is greater than that of chromium oxide alone.

Table I.—Dehydrocyclization of *n*-heptane; effect of iron oxide on chromium oxide

[500°C ., atmospheric pressure, L. H. S. V.=1, 5-hr. tests]

	Initial catalyst composition, mole percent		Number of catalyst regenerations	Av. toluene in liquid product, wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hour
	Cr_2O_3	Fe_2O_3				
100	0	0	0	22	15.5	0.7
100	0	1	1	20.5	14.5	0.65
90	10	0	0	11	10.5	0.6
90	10	1	1	7	7	0.4
80	20	0	0	9.5	9.5	0.55
80	20	1	1	8	7.5	0.45
70	30	0	0	24.5	22.5	1.35
70	30	1	1	20	18.5	1.1
60	40	0	0	30.5	28	1.65
60	40	1	1	26	24.5	1.45
50	50	0	0	27	24.5	1.45
50	50	1	1	25	23.5	1.4
30	70	0	0	14.5	14	0.85
30	70	1	1	14.5	13.5	0.8
0	100	0	0	3	3	0.08
0	100	1	1	1.5	1.5	0.045

This method of catalyst preparation is limited to the use of metal salts of monovalent anions which are decomposed completely during calcination. Such salts are nitrates and soluble organic salts such as acetates. Sulfates do not produce a satis-

factory sol unless the starch concentrations are made very high. The final catalysts so obtained, containing large amounts of sulfate ions, are of low activity. Chlorides cannot be used because the small amounts of chloride remaining in the catalysts act as serious catalyst poisons. Similarly, the precipitants are limited to ammonium hydroxide, sodium hydroxide and potassium hydroxide. Ammonium hydroxide is preferred because the ammonium ion is destroyed by calcination. Alkali carbonates cannot be used.

Other carbohydrates and polyalcohols may be substituted for the starch, such as glucose, cane sugar, or glycerol. Starch is preferred because it does not form a true solution in water and hence is not removed during the water-washing step. Consequently, the addition of starch provides a simple and easily controlled method not only for stabilization of the initial metal oxide sol but for prevention of oxidation of the chromium to hexavalent chromium during the calcination. Starch concentrations from about 25 grams to 200 grams per mol mixed metal nitrates in the initial stock solution may be used.

The concentration of metal salts in the initial stock solution may be varied from about 2 molar to 0.2 molar. The high concentrations are somewhat difficult to handle because of the high concentration of solids in the final slurry. The very low concentrations are inconvenient because of the large volumes of solution which must be handled.

EXAMPLE 2

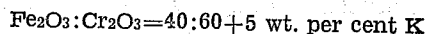
EFFECT OF HEAT TREATMENT ON IRON OXIDE-CHROMIUM OXIDE CATALYSTS

Catalyst preparation.—Five catalysts were prepared. The first three catalysts are part of a single preparation made similarly to the catalysts in Example 1. Mixed metal nitrates and soluble starch were converted into a sol and then rapidly precipitated at a pH of 8.0 ± 0.05 as described hereinbefore. After aging for 24 hours, the precipitate was separated by filtration and then subjected to quick freezing by dropping small portions into a large volume of kerosene maintained at about -20°C . by external cooling with dry ice and acetone. This quick freezing step was used to convert the gelatinous precipitate into a more granular form without loss of structure,

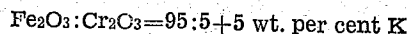
and then treated with 100 ml. of a saturated solution of ammonium sulfate for each gram mole of metal oxides present. This treatment replaced nitrate ions on the catalyst surface by sulfate ions without appreciably penetrating the interior of the hydrous oxide micelles. This addition of sulfate ions to the catalyst surface decreases oxidation of the chromium oxide during drying and also decreases coke formation during use of the final catalyst. After filtration and washing until the wash water showed no sulfate ions when tested with barium chloride, the precipitate was dried at 100°C . to 110°C . in an air-circulation drying oven.

The dried material was heat treated in successive steps of increasing severity at 500°C ., 600°C . and 800°C . A sample was removed for catalyst evaluation after each step of the heat treatment.

The last two catalysts were prepared from dry powders of C. P. commercial chemicals, using the procedure of Example 2, U. S. Patent No. 2,408,140. The catalyst designated



is similar in composition to the coprecipitated catalysts except for the addition of potassium. The catalyst designated



corresponds to the butylene dehydrogenation catalyst described in U. S. Patent No. 2,408,140. In both cases the dry metal oxides were mixed with the required amount of potassium carbonate dissolved in enough water to form a paste with the metal oxides and then 0.3 wt. per cent tannic acid was added. The paste was dried at 100°C . to 110°C ., formed into $\frac{1}{8}$ in. pellets, and these were calcined at 800°C . in a muffle furnace.

Catalyst evaluation.—The results are given in Table II. They show that the most active of these catalysts for *n*-heptane dehydrocyclization is the coprecipitated preparation heat treated at 500°C . The catalytic activity is diminished sharply for the higher temperatures of calcination, although measurable dehydrocyclization remains after a short heat treatment at 800°C . Neither of the catalysts prepared from dry powders in accordance with the method of U. S. Patent No. 2,408,140 shows perceptible activity for dehydrocyclization.

Table II.—Dehydrocyclization of *n*-heptane; effect of heat treatment on iron oxide-chromic oxide catalysts

[500°C ., atmospheric pressure, 5-hr. test periods]

Initial catalyst composition, mole percent	$\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=40:60$	$\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=40:60$	$\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=40:60$	$\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=40:60+5 \text{ wt. per cent K}$	$\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3=95:5+5 \text{ wt. per cent K}$
Catalyst preparation	Coprecipitation of nitrates by NH_4OH .	Coprecipitation of nitrates by NH_4OH .	Coprecipitation of nitrates by NH_4OH .	Metal oxide powders and K_2CO_3 .	Metal oxide powders and K_2CO_3 .
Heat treatment	4 hr. air at 500°C .	4 hr. air at 500°C ; 2 hr. air at 600°C .	4 hr. air at 500°C ; 2 hr. air at 600°C ; 2 hr. air at 800°C .	4 hr. air at 800°C .	4 hr. air at 800°C .
L. H. S. V.	0.75	0.75	1.0	1.0	0.75
Toluene in product, wt. percent	28.5	9.5	3	0	0
Av. conversion of heptane to toluene, wt. percent	25.5	9	3	0	0

thereby facilitating the washing step. The frozen material was allowed to thaw gradually,

These examples show that suitably prepared mixtures of iron oxide and chromium oxide are

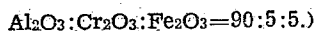
active for dehydrocyclization. However, such catalysts are not as stable to high temperatures as would be desired for commercial application. It has been found that this instability and tendency to sinter can be counteracted by the incorporation by coprecipitation of a refractory metal oxide such as alumina.

EXAMPLE 3

EFFECT OF ALUMINA IN COPRECIPITATED IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

Catalyst preparation.—These catalysts were prepared by rapid coprecipitation in the mixing device, described in Example 1. Starch was omitted from the preparations because dilution of the active metal oxides with relatively large amounts of oxides, such as alumina, which are not easily oxidized or reduced decreases the ease of oxidation of the chromium oxide during the drying stage. Oxidation during the calcination stage was avoided by heating in a stream of hydrogen instead of in air. The method is illustrated by the following:

A stock solution was prepared containing 0.45 mol $\text{Al}(\text{NO}_3)_3$, 0.025 mol $\text{Cr}(\text{NO}_3)_3$ and 0.025 mol $\text{Fe}(\text{NO}_3)_3$ per liter. (One liter of stock solution corresponded to 0.25 mol mixed oxides corresponding to the mol ratio



For each liter of this solution there was used approximately one liter of 1.5 molar NH_4OH . The two solutions were allowed to flow into the upper part of the mixing chamber mentioned in Example 1 and the rates of flow adjusted to produce a slurry with a pH of 8.5 ± 0.05 . This slurry was aged for 24 hours, filtered and the precipitate water-washed until the filtrate gave a negative test for nitrate ions with diphenylamine-sulfuric acid indicator. The filter cake was then dried in an air-circulation drying oven for about 18 hours and formed into $\frac{1}{8}$ in. pellets. The pelleted material was gradually heated to 300°C . in a hydrogen stream over an 8 hour period. The pellets were then heated further in a carbon dioxide stream for 8 hours while gradually increasing the temperature to 600°C ., after which the last traces of carbonaceous material were removed by passing air over the catalyst at 600°C .

Catalyst evaluation.—The dehydrocyclization activities of the once-regenerated catalysts are shown in Table III. In all cases the catalysts contained chromium oxide to iron oxide mol ratios, expressed as the sesquioxides, between 1:1 and 3:1.

Table III.—Dehydrocyclization of *n*-heptane; effect of alumina in coprecipitated iron oxide-chromium oxide-alumina catalysts

[500°C ., atmospheric pressure, L. H. S. V.=1, 5-hr. tests once-regenerated catalysts]

Initial catalyst composition, mol percent			Mol percent hydrogen in gas product	Av. toluene in liquid product, wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hr.
Al_2O_3	Cr_2O_3	Fe_2O_3				
90	5	5	88	14.5	13.5	0.8
80	10	10	93	15	14	0.85
70	15	15	93.5	25.5	23.5	1.4
70	20	10	92	24	22.5	1.35
60	30	10	92	28.5	25.5	1.5
50	30	20	92.5	41.5	36	2.1
30	35	35	92.5	45.5	39	2.3
30	28	42	91	54	30	1.8

From these data, it is concluded that:

(a) The high hydrogen contents of the gas products indicate the selectivity of the catalysts for dehydrogenation.

(b) The activity for dehydrocyclization is greater for the lower alumina concentrations but remains higher than that for the chromic oxide gel described in Example 1 up to and including 70 mol per cent alumina.

Within the range 30 to 70 mol per cent alumina, the catalysts show improved average activity and stability over parallel catalysts containing the same ratios of iron oxide and chromium oxide but in the absence of the alumina. Above 70 mol per cent alumina, the stability of the catalysts is excellent but the high dilutions with alumina cause the activity to drop off. Therefore, improved catalysts are obtained for alumina concentrations between 30 and 70 mol per cent, with the preferred concentrations within the range 30 to 50 mol per cent, the region of maximum activity and good stability.

EXAMPLE 4

EFFECT OF ALKALINE PROMOTERS ON THE ACTIVITY OF COPRECIPITATED IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

This example demonstrates the improved dehydrocyclization activity of iron oxide-chromium oxide-alumina catalysts when small amounts of alkaline promoters are added. It should be noted that the optimum amount of the promoters is less for *n*-heptane dehydrocyclization than for naphtha reforming. Since the normal promoter action of impregnated catalysts does not appear in fresh catalysts, only data for regenerated catalysts are given. Normal promoter action refers to the effect on catalytic activity after diffusion and reorientation of the catalyst surface has occurred. This readjustment of the promoted catalyst surface is not effected by heat treatment alone but is substantially complete after one cycle of on-stream and regeneration.

Catalyst preparation.—Three base catalysts were prepared according to the method described in Example 3. The promoted catalysts were obtained by adding the calculated amount of the nitrate of the promoter metal to a part of the base catalyst. The metal nitrates were dissolved in just enough water such that the solution would be absorbed completely by the catalyst and the solution was added with thorough mixing in order to obtain uniform absorption. After drying for about 18 hours at 75°C . in an air-circulation drying oven, the impregnated catalysts were heated in an air stream over an 8-hour period with the temperature gradually raised to 600°C . and then maintained at this temperature for 4 hours. This treatment decomposed the nitrates to the corresponding oxides.

Catalyst evaluation.—The pertinent data are given in Table IV. These data show that the addition of from 1 to 2 atomic percent of sodium, potassium, calcium, strontium or cerium improves the catalytic activity. It should be noted that the addition of both copper and potassium is more effective than either promoter when used alone at the same concentration.

Table IV.—Dehydrocyclization of *n*-heptane; coprecipitated iron oxide-chromium oxide-alumina catalysts impregnated with alkaline promoters

[500°C., atmospheric pressure, L. H. S. V.=1, 5-hr. tests once-regenerated catalysts]

Initial composition of catalyst base, mol percent			Promoter, atomic percent based on initial mixed oxide base	Av. toluene in liquid product, wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hr.
Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃				
50	30	20	None	26	24	1.4
50	30	20	2 sodium	29	27	1.6
50	30	20	1 potassium	32	29	1.7
50	30	20	2 potassium	34.5	32	1.85
50	30	20	3 potassium	24.5	23	1.3
50	30	20	1 calcium	28	26	1.55
50	30	20	2 calcium	34	31	1.8
50	30	20	3 calcium	29.5	27	1.6
50	30	20	1 strontium	31	28	1.65
50	30	20	2 strontium	34	31	1.8
50	30	20	0.5 copper	25	25	1.5
50	30	20	3 potassium + 0.5 copper	32.5	30	1.75
50	30	20	1 cerium	28	25.5	1.5
70	15	15	None	19	17.5	1.05
70	15	15	3 potassium	24	23	1.35
30	42	28	None	30.5	27	1.6
30	42	28	1 potassium	38	33	1.9

The requirement of the supports is that they must have relatively high surface areas, they should have only negligible cracking activity and they must be heat-stable. "Porocel," or calcined bauxite, is an inexpensive form of alumina which satisfies these minimum requirements. The so-called activated aluminas and gel-type alumina have structural characteristics which produce superior catalysts for dehydrocyclization reactions.

The basic requirements for impregnation of a suitable catalyst support such as alumina are that the metal salts used form true solutions in water, do not hydrolyze to form insoluble materials in contact with the catalyst support, and decompose to form only the active metal oxides upon calcination. The first two requirements are necessary in order to obtain uniform impregnation and to prevent preferential diffusion into the interior of the catalyst. These requirements are met by using an acid solution of metal nitrates or salts of organic acids such as acetic acid. If the impregnation solution is not acid, there is a tendency for a preferential migration of hydrogen ions into the interior of the catalyst with hydrolysis of the iron group metal salt. This leads to the formation of an iron group metal oxide coating near the outer surface of the catalyst support, hence a non-uniformly impregnated support.

EXAMPLE 5

ALUMINA-SUPPORTED IRON OXIDE-CHROMIUM OXIDE CATALYSTS

Catalyst preparation.—The simplest and preferred solution for impregnation consists of ferric nitrate, chromic acid and potassium nitrate in amounts selected to form the required ratio of active oxides after calcination. These salts are dissolved in just enough water to be absorbed by the catalyst support. The solution is added to the support in such a manner to moisten it uniformly, and the material dried on a steam bath or air bath. The product is then heated gradually in a stream of air over an 8-hour period to 600° C. to decompose the metal nitrates and chromic acid.

Catalyst evaluation.—These catalysts show a change in activity after the first regeneration,

the change usually being to higher activity, indicating a reorientation of the catalyst surface which is not effected by heat alone. This change is practically complete after the first regeneration, as shown by substantially constant activity after subsequent regenerations. The data in Table V are for the once-regenerated catalysts.

Table V.—Dehydrocyclization of *n*-heptane; alumina-supported iron oxide-chromium oxide; initial composition of active oxides Fe₂O₃:Cr₂O₃—40:60 (mol ratio)+1 atomic percent K

[500° C., atmospheric pressure, L. H. S. V.=1, 5-hr. tests once-regenerated catalysts.]

Type of alumina support	Active oxides, wt. percent of support	Av. toluene in liquid product, wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hour
Low-SiO ₂ , low iron "Porocel"	10.5	17	16	0.85
"Alorco-F-1, Activated Alumina"	10.5	29	27	1.6
Harshaw Chem. Co. Activated Alumina	13.5	21	20	1.5
Harshaw Chem. Co. "Uvergel" alumina	10.5	19.5	18	1.35

The results show that all of the alumina-base supports are satisfactory for dehydrocyclization. Calcined bauxite, or "Porocel" is the least satisfactory, probably because of the amount of silica which it contains. The commercial activated alumina and the gel-type alumina known as "Uvergel" produced catalysts comparable in activity to the coprecipitated catalysts described in Example 4.

An activating support is preferred for these catalysts. An activating support is defined as one which has substantially no catalytic action itself but which has a surface structure such that when impregnated with metal oxides active for dehydrocyclization forms catalysts which are more active than can be accounted for solely by composition and surface area of the catalyst. While the mechanism of such activation is not clearly understood, the distinction between activating and non-activating alumina supports is well known to the art of catalyst preparation.

EXAMPLE 6

EFFECT OF ASSOCIATED IONS ON THE COPRECIPITATION OF IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

This example demonstrates the influence of associated ions, both in regard to promoter action and without promoter action, on dehydrocyclization activity.

Catalyst preparation.—Catalyst No. 1 is the datum of comparison for the remaining catalyst. It was the same catalyst described in Example 4, prepared by rapid coprecipitation of the mixed metal nitrates with NH₄OH.

Catalyst No. 2 was similar to catalyst No. 1, except that it was prepared by rapid coprecipitation of mixed metal nitrates with potassium carbonate. A stock solution was prepared containing 0.25 mol Al(NO₃)₃, 0.15 mol Cr(NO₃)₃ and 0.10 mol Fe(NO₃)₃. (One liter of stock solution corresponded to 0.25 mol mixed oxides in the mol ratio Al₂O₃:Cr₂O₃:Fe₂O₃=50:30:20.) Six liters of this solution were added slowly to a vigorously stirred solution of 4.6 mols K₂CO₃ (a slight excess) dissolved in 12 liters of water. The evolution of carbon dioxide caused the pH of the slurry to drop to about 6.5 during the precipita-

tion. After the addition of the metal salts was complete, the pH was raised to 8.5 by the addition of 6 N KOH. After aging for 24 hours, the slurry was filtered and the precipitate quick-frozen as described in Example 3. After allowing to thaw gradually, there was added to the

Catalyst evaluation.—The results are given in Table VI. They show that all of these methods of catalyst preparation were satisfactory and that the catalysts had a dehydrocyclization activity greater than that of the chromic oxide gel described in Example 1.

Table VI.—Dehydrocyclization of *n*-heptane, iron oxide-chromium oxide-alumina catalysts coprecipitated at pH of 8.5

[500° C., Atmospheric pressure, L. H. S. V.=1, 5-hr. tests, once-regenerated catalysts]

Catalyst No.	Initial composition of catalyst base, mol percent			Reagents for coprecipitation	Promoters, atomic percent of initial mixed oxide base		Av. toluene in liquid product, wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hr.
	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃		K	Cu			
1	50	30	20	Mixed metal nitrates and NH ₄ OH	0	0	26	24	1.4
2	50	30	20	Mixed metal nitrates and K ₂ CO ₃	10.3	0	34	28.5	1.65
3	50	30	20	Mixed metal nitrates and K ₂ CO ₃	16.8	0	30.5	27	1.6
4	30	42	28	Mixed metal nitrates and NH ₄ OH	0	0	30.5	27	1.6
5	30	42	28	Mixed metal nitrates and NH ₄ OH	21	0	38	33	1.9
6	30	42	28	Mixed metal nitrates and NH ₄ OH	21	0.5	34	30	1.75
7	30	42	28	Mixed metal sulfates and NH ₄ OH	1.3	0.16	29.5	26.5	1.55

¹ Promoter concentration obtained by incomplete removal of potassium carbonate used for precipitation.

² Promoter aided by impregnation of calcined metal oxides with metal nitrates of promoter metals.

³ Metal sulfates consisting of ferric sulfate, aluminum sulfate and chromium-potassium sulfate.

slurry 100 ml. of a saturated solution of ammonium sulfate per mol equivalent of the precipitated metal oxides; i. e., 150 ml. ammonium sulfate solution for the batch. The precipitate was filtered off and water-washed until neither carbonate nor sulfate ions could be detected in the wash water. The wet cake was then dried, pelleted, and calcined, exactly as described for catalyst No. 1. The calcined catalyst contained 0.3 atomic per cent potassium as determined by flame spectrophotometry. (0.3 atomic per cent K represents 0.003 gram atom K for 1 mol catalyst or 0.5 mol Al₂O₃+0.3 mol Cr₂O₃+0.2 mol Fe₂O₃.) This potassium originated from the potassium carbonate used to effect the coprecipitation.

Catalyst No. 3 was prepared like catalyst No. 2 except that the washing was discontinued after only partial removal of carbonate and sulfate. This resulted in a finished catalyst containing 6.8 atomic per cent potassium, based on the heavy metal oxides, as determined by flame spectrophotometry.

Catalyst No. 4 was prepared like catalyst No. 1 except that the ratio of aluminum, chromium and ferric nitrates was altered to produce the indicated mol ratios of metal oxides in the finished catalyst.

Catalysts Nos. 5 and 6 were portions of catalyst No. 4 which, after calcination, were impregnated with metal nitrates exactly as described in Example 4.

Catalyst No. 7 was prepared exactly like catalyst No. 5 except that metal sulfates were substituted for the metal nitrates. The availability of potassium chrome alum led to its use in place of the more difficultly obtainable water-soluble chromic sulfate. This catalyst was washed in a brass-lined centrifuge instead of in the usual porcelain filters. The dried and calcined product was impregnated with potassium nitrate in an amount calculated to produce 1 atomic per cent potassium based on the metal oxides. Flame spectrophotometry indicated a slightly higher potassium content, the additional potassium presumably having been retained by adsorption from the potassium chrome alum solution used in the catalyst preparation. The small amount of copper originated from the brass liner for the centrifuge basket.

EXAMPLE 7

EFFECT OF TEMPERATURE AND CHARGE RATE ON THE DEHYDROCYCLIZATION OF *n*-HEPTANE WITH IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

These tests were carried out with the catalyst No. 3 described in Example 6, in order to show the effect of temperature and charge rate on toluene formation. This catalyst was selected because it showed the marked induction period which characterizes highly promoted catalysts of this invention when they are tested in the manner described.

The variation in activity with time for various temperatures when operating at a L. H. S. V. of 0.5 is shown graphically in Figure 3. The points represent the toluene content of hourly samples. By placing these values at the mid-points of the period over which they were collected, and drawing a smooth curve through them, a reasonably accurate picture of the variation of catalytic activity over the entire period is obtained.

The curves in Figure 3 indicate a marked induction period, the length of which decreased with rising temperature. In each case the extrapolated curves indicated a substantially zero conversion at the beginning of the test. At 485° C., the maximum catalytic activity was not reached during the 5-hour test period. The time required to reach a maximum decreased from about 3.5 hours at 500° C. to 1.5 hours at 525° C. The maximum toluene content of the product at 525° C. was about 83 wt. per cent.

The average values for the 5-hour test periods are given in Table VII. For operations at an L. H. S. V. of 0.5, the average toluene content of the product and average conversion of heptane to toluene increased as the temperature was raised from 485° C. to 525° C. For this charge rate, cracking to gaseous hydrocarbons did not become serious at 525° C. The effect of temperature on the conversion of heptane to toluene and on the rate of toluene formation, expressed as gallons of toluene per cu. ft. of catalyst per hour, is shown graphically in Figures 4 and 5.

The effect of charge rate at constant temperature is shown by a comparison of the three tests made at 500° C. at different space velocities. As would be expected, the average conversion of

n-heptane to toluene decreased as the charge rate was increased from L. H. S. V.=0.5 to L. H. S. V.=1.0. However, the rate of toluene formation in terms of the unit volume of catalyst increased over the range of charge rates tested.

Table VII.—Dehydrocyclization of n-heptane; effect of temperature and charge rate; initial catalyst composition: $\text{Fe}_2\text{O}_3:\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3$ —20:30:50 (mol ratio) +6.8 atomic percent K from mixed metal nitrates and K_2CO_3

[Atmospheric pressure, 5-hr. tests, once-regenerated catalysts]

Temp., ° C.	L. H. S. V.	Av. toluene in liquid prod., wt. percent	Av. conversion of heptane to toluene, wt. percent	Av. gal. toluene per cu. ft. catalyst per hour
485	0.5	14	13	0.4
500	0.5	44	37	1.1
515	0.5	58	46	1.35
525	0.5	64.5	49	1.45
500	0.75	30.0	27	1.2
500	1.0	30.5	27	1.6

From the foregoing, it is concluded that:

(a) In order to obtain high concentrations of toluene in the product, severe conditions, of the order of 515° C. or higher and low space velocities such as L. H. S. V. of 0.5 or less, are to be preferred;

(b) In order to obtain greatest catalyst efficiency with moderate conversions to toluene, milder conditions, such as 500° C. and L. H. S. V. of 1.0, should be used; and

(c) Within reasonable limits, increasing temperatures and decreasing charge rates have the same effect in increasing the formation of toluene.

EXAMPLE 8

REPLACEMENT OF IRON BY COBALT OR NICKEL IN IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

This example demonstrates the effect of substitution of atomic equivalents of cobalt or nickel for iron in iron oxide-chromium oxide-alumina catalysts. While most of the experimental work has been concentrated on the iron-containing catalysts because of the inexpensiveness of the iron compounds, it is evident that the cobalt- and nickel-containing catalysts are equal to or better than those containing iron.

The catalysts are formulated as mixtures of the sesquioxides. This is merely a matter of convenience for representing substitution of atomic equivalents of the iron group metals. While the iron-containing catalysts were prepared from ferric salts, which form the sesquioxide directly, the cobalt and nickel catalysts were prepared from salts of the divalent metals which do not form the sesquioxides by simple precipitation methods. Since the valence states corresponding to the active metal oxides cannot be specified, an arbitrary formulation is unavoidable.

Catalyst preparation.—The iron-containing catalyst in Series A was that described in Examples 6 and 7, obtained by the potassium carbonate precipitation of mixed metal nitrates. The iron-containing catalyst in Series B was the third catalyst in Table III, prepared by coprecipitation of the metal nitrates with ammonium hydroxide. The cobalt- and nickel-containing catalysts were obtained by methods exactly similar to those used for the iron-containing catalysts by substituting cobalt or nickel nitrate for the ferric nitrate.

Catalyst evaluation.—The results are summarized in Table VIII. From these data it will be seen that the dehydrocyclization activity of these catalysts increases in the order iron to cobalt to nickel, for the combinations with chromium oxide and alumina.

ized in Table VIII. From these data it will be seen that the dehydrocyclization activity of these catalysts increases in the order iron to cobalt to nickel, for the combinations with chromium oxide and alumina.

Table VIII.—Dehydrocyclization of n-heptane; replacement of iron by cobalt or nickel in iron oxide-chromium oxide-alumina catalysts (once regenerated catalysts)

Iron group metal		Iron	Cobalt	Nickel
15	A. Catalysts prepared by potassium carbonate precipitation of mixed metal nitrates containing metal ions in the ratio group metal: chromium: aluminum=20:30:50:			
	L. H. S. V.-----	0.5	1.0	1.0
	Av. toluene in liquid prod., wt. percent-----	14	22	33.5
20	Av. conversion of heptane to toluene, wt. percent-----	13	17	30
	Av. gal. toluene per cu. ft. catalyst per hour-----	0.4	1.0	1.75
25	B. Catalysts prepared by ammonium hydroxide precipitation of mixed metal nitrates containing metal ions in the ratio iron group metal: chromium: aluminum=15:15:70:			
	Av. toluene in liquid prod., wt. percent-----	25.5	37	32
	Av. conversion of heptane to toluene, wt. percent-----	23.5	30	26.5
30	Av. gal. toluene per cu. ft. catalyst per hour-----	1.4	1.75	1.55

¹ Tests at 485° C., atmospheric pressure, 5-hour periods.

² Tests at 500° C., atmospheric pressure, 5-hour periods, L. H. S. V.=1.0.

EXAMPLE 9

REFORMING LIGHT PARAFFINIC NAPHTHA WITH COPRECIPITATED METAL OXIDE CATALYSTS

This example illustrates the aromatization-reforming activity of iron oxide-chromium oxide combinations which are active for n-heptane dehydrocyclization. The naphtha charge was a hexane-heptane fraction of a Mid-Continent stock containing relatively large proportions of branched-chain paraffins. It is representative of a low sulfur, paraffinic stock which is difficult to reform by thermal or catalytic methods.

Catalyst preparation.—The iron oxide-chromium oxide catalyst was the preparation of this composition described in Example 1, obtained by coprecipitation of the metal nitrates with ammonium hydroxide. The remaining two catalysts were prepared in the manner described for catalyst No. 7 in Example 6, from mixed metal sulfates and ammonium hydroxide. Sulfates were used because of the availability of zirconium and titanium sulfates as contrasted with the difficulty of obtaining the metal nitrates.

Catalyst evaluation.—The results are summarized in Table IX. The data in Table IX are average values for three successive 2-hour test periods, with air-regeneration of the catalysts between each test period. The high octane numbers of the unstabilized liquid products and the high liquid recovery, compared to thermal reforming, indicate the advantages of aromatization reforming with these catalysts.

It has been pointed out that the iron oxide-chromium oxide combinations are active but unstable at high temperatures. Since conditions of naphtha reforming and oxidative regeneration are considerably more severe than those required for n-heptane dehydrocyclization, this example shows that the iron oxide-chromium oxide combinations are active even under conditions of mild sintering. The catalysts containing zirconium

nium oxide and titanium oxide represent catalysts in which the coprecipitated refractory support is non-activating; i. e., it improves the stability but not the dehydrocyclization activity of the active metal oxides.

3. Example 6. Additional promoters were added to the calcined catalyst by impregnation, as indicated in Table X.

Catalyst evaluation.—The results of the catalyst evaluations are shown in Table X.

Table IX.—Reforming light paraffinic naphtha¹ with coprecipitated metal oxide catalysts

[538° C. (1000° F.), atmospheric pressure, L. H. S. V.=1, Av. values for three 2-hr. test periods]

Initial composition of catalyst, mol percent	Fe ₂ O ₃ :Cr ₂ O ₃ =40:60	Fe ₂ O ₃ :Cr ₂ O ₃ :ZrO ₂ =20:30:50	Fe ₂ O ₃ :Cr ₂ O ₃ :TiO ₂ =20:30:50
C. F. E. R.—Clear-octane No. of unstabilized liquid product	73	73	75
Hydrogen content of gas products, mol percent	80.5	80	81.5
Products (based on 100 wt. percent recovery):			
C ₃ -free gasoline, vol. percent	85.5	87	84.5
Dry gas, wt. percent	7.8	5.9	6.7
Coke, wt. percent	4.4	4.9	6.8

¹ Charge.—Oklahoma City naphtha:

A. S. T. M. distillation: I. B. P. 160° F., 10% at 175, 50% at 194, 90% at 222, E. P. 262° F.
A. P. I. gravity 65.3°
Reid vapor pressure 2.9 lb.
Sulfur 0.012 wt. percent.
Octane No., clear:
C. F. R. R. 58.8
C. R. F. M. 57.0

EXAMPLE 10

REFORMING LIGHT PARAFFINIC NAPHTHA WITH IRON OXIDE-CHROMIUM OXIDE-ALUMINA CATALYSTS

This example illustrates various methods for preparing active reforming catalysts by coprecipitation of iron oxide and chromium oxide with an activating refractory oxide, i. e., alumina.

Catalyst preparation.—These catalysts were prepared by rapid precipitation of mixed metal salts with an alkaline solution as described in Example 6.

The catalyst preparation from metal sulfates and ammonium hydroxide was made in the manner described for catalyst No. 7, Example 6.

The catalyst preparations from metal nitrates and ammonium hydroxide were made in the manner described for catalysts No. 5 and 6 of Example 6, the promoters being added by impregnation of the calcined metal oxide preparations.

Comparing catalysts 1, 2 and 4, it will be observed that the activity of the catalysts, as shown by the research octane number of the unstabilized liquid products, increased in the order named. Catalyst No. 2, prepared from the metal nitrates and promoted with a small amount of potassium, showed the highest yield and lowest coke formation for this group of three catalysts.

Catalyst No. 3 was a part of the catalyst base used to prepare catalyst No. 2 in which the promoter concentration was increased to 7 atomic per cent potassium by impregnation with potassium acetate in order to approximate the analysis of catalyst No. 4. While catalyst No. 3 was a satisfactory reforming catalyst, it was less active than catalyst No. 2, which was impregnated with a small amount of potassium, and it was less active than catalyst No. 4 which had closely the same amount of potassium.

Table X.—Reforming light paraffinic naphtha¹; initial composition of catalyst base: Fe₂O₃:Cr₂O₃:Al₂O₃=20:30:50 mol ratio atmospheric pressure

Catalyst N	1	2	3	4	5	6	7
Catalyst preparation	Metal sulfates copptd. by NH ₄ OH	Metal nitrates copptd. by NH ₄ OH	Metal nitrates copptd. by NH ₄ OH	Metal nitrates copptd. by K ₂ CO ₃	Metal nitrates copptd. by K ₂ CO ₃	Metal nitrates copptd. by K ₂ CO ₃	Metal nitrates copptd. by K ₂ CO ₃
Promoter atomic percent based on initial mixed oxides	None	1.1 K, by impregnation with KNO ₃	7 K, by impregnation with KOAc	6.8% K, from K ₂ CO ₃ precipitant	6.8% K, from K ₂ CO ₃ ; 2 K by KNO ₃ impregnation ²	6.8% K from K ₂ CO ₃ ; 2 Cu by CuNO ₃ impregnation ²	6.8% K from K ₂ CO ₃ ; 1 Ba by BaNO ₃ impregnation ²
Test conditions:							
Temperature, ° F.	1000	1000	650	1000	1000	1000	1000
L. H. S. V.	1	1	0.5	1	1	1	1
Test period, hr.	2	5	5	2	2	2	2
Number of periods, averaged	3	2	2	3	3	3	3
Properties of unstabilized liquid product:							
Micro-Reid vapor press., lb.	2.7	2.6	23.7	3.9	2.0	2.5	
Norwood bromine No.	17.4	23.1	23.7	23.8	23.8	20.6	
Micro-octane No.—Clear:							
C. F. R. R.	74.5	75.5	75.5	79	78.5	75	76
C. F. R. M.				73	71	69	
Products (based on 100 wt. percent recovery):							
C ₃ -free gasoline, vol. percent	86.5	89.5	87.3	85.6	84.7	88.7	90.6
Dry gas, wt. percent	4.9	4.9	6.1	5.5	8.1	5.4	5.8
Coke, wt. percent	4.7	2.2	5.6	6.3	4.5	3.6	2.4

¹ Oklahoma City naphtha; same charge as in Table IX.

² Total K 8.8 atomic percent of mixed oxides.

The catalyst prepared from metal nitrates and potassium carbonate were a part of catalyst No.

In view of the foregoing, it may be concluded:
(a) Catalysts used for aromatization reform-

ing are less sensitive to changes in promoter concentration than similar catalysts used for n-heptane dehydrocyclization; cf. Example 4.

(b) The optimum promoter concentration is less when the promoter is added by impregnation than when it is incorporated during the coprecipitation, as in the case of catalyst No. 3.

This second conclusion is strengthened by the results obtained with catalyst No. 5, prepared by impregnating catalyst No. 4 with an additional 2 atomic per cent potassium to obtain a total of 8.8 atomic per cent potassium in the catalyst. Catalyst No. 5 was only slightly less active than catalyst No. 4 and much more active than catalyst No. 3.

Without any intent of limiting the scope of the present invention, it is postulated that the effect of the alkaline promoters in aromatization reforming is twofold. The effect of alkali incorporated within the catalyst particles, as in catalyst No. 4, is predominantly one of improving the structural stability. This beneficial effect is obtained for a wide range of concentrations of the alkali and alkaline earth metals up to about 10 atomic per cent of the alkaline promoter. In addition to this effect, it appears desirable to have a small and more critically limited amount of promoter on the catalyst surface, such as that obtained by impregnation with 1 or 2 atomic per cent of the promoter metal. This surface alkali improves the adsorptive and desorptive behavior of the catalyst surface. There appears to be a limited migration of the promoter metal ions on the catalyst surface and a limited diffusion from the surface into the interior of the catalyst, as shown by the change in activity, usually an increase in activity, after the first regeneration.

This influence of small amounts of alkaline substances on the catalyst surface is illustrated in catalyst No. 4 to 7, inclusive, all of which were prepared from catalyst No. 4 as a base. In catalyst No. 4, the relatively large amounts of alkali were largely fixed within the catalyst structure. The further addition of 2 per cent potassium, 2 per cent copper or 1 per cent barium by impregnation decreased the octane number of the product only slightly but decreased the coke formation sharply. This decrease in coke formation is particularly important where rapid regeneration of the catalysts by air oxidation without excessive heat liberation is required.

EXAMPLE 11

REFORMING MIDDLE EAST NAPHTHAS

The preceding examples have been concerned with reforming a hexane-heptane fraction of a Mid-Continent paraffinic naphtha. This example illustrates the results obtained with less refractory stocks.

The "Uvergel" supported catalysts were the same as the last catalyst in Example 5. The coprecipitated catalyst was prepared exactly like catalyst No. 2 in Example 10 except that the promoter concentration was increased to 2 atomic per cent potassium.

The mixed Iranian naphtha was a hexane-heptane fraction of a Middle East crude while the Gach Saran naphtha was essentially a 250 to 400° F. boiling range fraction of a Middle East crude. The results are summarized in Table XI.

The data in Table XI show that both the supported and coprecipitated catalysts gave better results with these stocks than those obtained with the light, Mid-Continent naphtha. A comparison of the octane-yield-coke figures in Table XI shows that the coprecipitated catalysts gave better results with both naphthas.

Table XI.—Reforming Middle East naphthas, potassium-iron oxide-chromium oxide-alumina catalysts

[538° C. (1000° F.), atmospheric pressure, L. H. S. V.=1]

	Catalyst			
	Impregnated, 0.75 moles (Fe ₂ O ₃ :Cr ₂ O ₃ =40:60+1%K) per 100 g. "Uvergel" alumina		Coprecipitated, metal nitrates and NH ₄ OH; Fe ₂ O ₃ : Cr ₂ O ₃ :Al ₂ O ₃ = 20:30:50+2%K	
Naphtha charge.....	Light ¹	Heavy ²	Light ¹	Heavy ²
C. F. R. R. clear octane No. of charge.....	56	42.5	56	42.5
Properties of unstabilized liquid Product:				
Norwood bromide No.....	22.4	20.3	21.3	23.1
Micro-octane No., C. F. R. R.—Clear.....	83.5	87	85	86
Products (based on 100 wt. percent recovery):				
C ₃ -free gasoline, vol. per cent.....	81.8	76.8	81.7	81.7
Dry gas, wt. percent.....	7.4	11.0	7.4	7.4
Coke, wt. percent.....	7.7	9.0	6.7	7.8

¹ Light naphtha, mixed Iranian. A. S. T. M. distillation: I. B. P. 121° F., 10% at 161°, 50% at 212°, 90% at 267°, F. B. P. 311° F.
² Heavy naphtha, Gach Saran. A. S. T. M. distillation: I. B. P. 248° F., 10% at 276°, 50% at 312°, 90% at 365°, F. B. P. 395° F.

EXAMPLE 12

REFORMING PARAFFINIC LIGHT NAPHTHA WITH ALUMINA-SUPPORTED CATALYSTS

Catalyst preparation.—The three catalysts were prepared by the same procedure. One liter-
portions of the catalyst supports ("Uvergel" or "Porocel" alumina) were impregnated with 0.15 mol potassium carbonate dissolved in enough water to moisten the support. The amount of potassium carbonate was selected to produce 0.03 gram atom of potassium per 100 cc. support. The impregnated support was dried for about 18 hours at 75° C. in an air-circulation drying oven, then heated gradually in a muffle furnace over a 6-hour period to 600° C. and then maintained at this final temperature for 4 hours. After cooling, the potassium-impregnated supports were impregnated with solutions of mixed metal nitrates calculated to produce 0.1 mol of mixed metal oxides per 100 cc. of support. The reimpregnated materials were then dried and recalcined as described for the potassium impregnation. The products then contained 0.1 mol of catalytically active metal oxides promoted with 3 atomic per cent K per 100 cc. of support (or 30 atomic per cent K based on the active metal oxides).

Catalyst evaluation.—The results obtained with these catalysts, summarized in Table XII, show that both the iron- and cobalt-containing catalysts had exceptionally good activity for aromatization-reforming of light paraffinic naphtha.

Table XII.—Reforming paraffinic light naphtha¹
with alumina-supported catalysts

Supported metal oxides	Fe ₂ O ₃ :Cr ₂ O ₃ = 40:60+30% K. "Uvergel"	Co ₂ O ₃ :Cr ₂ O ₃ = 40:60+30% K. "Uvergel"	Co ₂ O ₃ :Cr ₂ O ₃ = 40:60+30% K. "Porocel"
Support	alumina.	alumina.	alumina.
Amount of supported metal oxides	0.1 Mol per 100 cc. support.	0.1 Mol per 100 cc. support.	0.1 Mol per 100 cc. support.
Test conditions:			
Temperature, ° F.	950.	1,000.	950.
L. H. S. V.	0.5.	1.0.	0.5.
Test period, hr.	5.	5.	2.
Number of test periods, averaged	3.	2.	6.
Properties of unstabilized liquid product:			
Norwood bromine No.	26.2.	28.7.	26.8.
Micro-octane No., C. F. R. R.—Clear	80.	78.5.	79.5.
Products (based on 100 wt. percent recovery):			
C ₃ -free gasoline, vol. percent	86.9.	86.8.	89.7.
Dry gas, wt. percent	5.5.	6.5.	3.6.
Coke, wt. percent	5.8.	4.25.	5.3.

¹ Oklahoma City naphtha; same charge as in Table IX.

EXAMPLE 13

This example illustrates the use of catalysts of this invention under conditions of steam dilution. The steam dilution decreases the average coke formation and thereby prolongs the onstream period between regenerations. In order to counteract the adverse effect of water vapor on the dehydrocyclization of paraffins [cf. Mattox, J. Am. Chem. Soc. 66, 2059 (1944)], the operating temperatures must be increased.

Catalyst preparation.—Catalyst No. 1 was identical with catalyst No. 5, Example 10; catalyst No. 2 was identical with catalyst No. 5, Example 6; catalyst No. 3 was identical with catalyst No. 1, Example 12; catalyst No. 4 was identical with catalyst No. 2, Example 12.

Catalyst evaluation.—The average results for duplicate 10-hour test periods are shown in Table XIII. The yields of C₃-free gasoline were superior to those obtained in the absence of water. This increase in yield for substantially the same octane number was partly a result of the lower coke formation and also because of the higher olefin formation in the presence of an inert diluent such as steam.

25

EXAMPLE 14

REFORMING DEPENTANIZED LIGHT NAPHTHA WITH HYDROGEN DILUTION

This example illustrates the superiority of the catalysts of this invention over a typical "hydroforming" catalyst. The molybdena-alumina hydroforming catalyst was a commercially available catalyst which is exceptionally active for reforming under hydrogen pressures. The iron oxide-chromium oxide-alumina catalyst was obtained by potassium carbonate precipitation of mixed metal nitrates, and is identical with the catalyst of the same composition discussed in Examples 6, 7 and 10.

Catalyst evaluation.—The conditions of the catalyst tests were adjusted to obtain liquid products of substantially the same research octane number. In both series of tests, the total pressure was 150 p. s. i. g., and the hydrogen to hydrocarbon mol ratios were 5:1. The results are summarized in Table XIV. It is evident from the data in Table XIV that the iron-containing catalyst gave a better liquid recovery than the hydroforming catalyst for the same octane number. This improved liquid recovery resulted partly

30

35

40

45

Table XIII.—Reforming paraffinic light
naphtha¹ with steam dilution

[593° C. (1100° F.), atmospheric pressure, L. H. S. V.=1, 33 mol percent steam in charge; 10-hour test periods, Av. of 2 tests]

Catalyst	Properties of unstabilized products.			Products, based on 100 wt. percent recovery		
	Norwood bromine No.	C. F. R. R. octane No.	Reid vapor press.	C ₃ -free gasoline, vol. percent	Dry gas, wt. percent	Coke, wt. percent
Fe ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 (Mol Ratio)+8.8% K mixed metal nitrates coprecipitated by NH ₄ OH; impregnated with KOAc.	25.6	75	4.0	87	11.5	1.1
Fe ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =28:42:30 (Mol Ratio)+1% K; mixed metal nitrates coprecipitated by NH ₄ OH; impregnated with KNO ₃ .	32.5	73.5	4.5	90	7.2	1.4
0.1 Mol (Fe ₂ O ₃ :Cr ₂ O ₃ =40:60) on 0.03 gram atoms K on 100 cc. "Uvergel" alumina.	34.0	78.5	3.3	78.5	11.75	2.0
0.1 Mol (Co ₂ O ₃ :Cr ₂ O ₃ =40:60 on 0.63 gram atoms K on 100 cc. "Uvergel" alumina.	32.6	78.5	3.2	88.5	9.15	1.5

¹ Oklahoma City naphtha; substantially the same as charge in Table IX; C. F. R. R. Octane No. 59.5.

from the lower gas formation and partly from the higher olefin content of the gasoline obtained with the iron oxide-chromium oxide-alumina catalyst.

Table XIV.—Reforming paraffinic light naphtha¹ with hydrogen dilution

[Av. values for three 5-hr. test periods]

	Catalyst	
	Harshaw Chem. Co. 10% MoO ₃ on "Uver-gel" alumina	Fe ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 mol ratio + 6.8 K, co-precipitated from metal nitrates by K ₂ CO ₃
Test conditions:		
Temperature, ° C.	490	538
Pressure, p. s. i. g.	150	150
L. H. S. V.	0.66	0.55
Dilution, mols H ₂ /mol charge	5	5
Properties of unstabilized liquid product:		
Reid vapor pressure, lb.	6.6	7.7
Norwood bromine No.	0.6	13.7
Micro-octane No.—Clear:		
C. F. R. R.	81.5	82
C. F. R. M.	76	75
Products—based on 100 wt. percent recovery:		
C ₂ -free gasoline, vol. percent.	81.5	88
Dry gas, wt. percent.	15.5	8.1
Coke, wt. percent.	0.6	1.4

¹ Oklahoma City naphtha; same charge as in Table IX.

EXAMPLE 15

DESULFURIZATION OF PARAFFINIC LIGHT NAPHTHA

This example illustrates the desulfurization of naphtha containing high concentrations of refractory sulfur compounds. It is well known that organic sulfur compounds such as mercaptans and disulfides are easily removed or decomposed by catalysts of low activity such as clay and bauxite. However, the refractory sulfur compounds such as thiophene are not affected by such treatments. Therefore, desulfurization of a naphtha containing relatively high concentrations of thiophenic sulfur illustrates the effectiveness of the catalysts of this invention for removal of the more difficultly removable sulfur compounds.

The iron-containing catalyst was identical with that used in Example 14. The cobalt-containing catalyst was identical with the cobalt-containing catalyst in Table VIII-A.

Catalyst evaluation.—The catalyst evaluation conditions were substantially the same as those used for aromatization reforming in the presence of hydrogen. The liquid products were caustic-washed in order to remove dissolved hydrogen sulfide before obtaining octane numbers. The results are summarized in Table XV.

Table XV.—Desulfurization of paraffinic light naphtha¹

	Catalyst	
	Fe ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 + 6.8 K; mixed metal nitrates co-precipitated by K ₂ CO ₃	Co ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 mixed metal nitrates co-precipitated by K ₂ CO ₃
Test conditions:		
Temperature, ° F.	1,000	950
Temperature, p. s. i. g.	150	150
Dilution, mols H ₂ /mol charge	5	5
Test period, hr.	5	5
Properties of unstabilized liquid product:		
Reid vapor pressure, lb.	5.3	4.4
Norwood bromine No.	21.7	15.3
Total sulfur, wt. percent.	0.035	0.025
Micro-octane No., C. F. R. R.—Clear.	69.5	66.5

Table XV.—Desulfurization of paraffinic light naphtha¹.—Continued.

	Catalyst	
	Fe ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 + 6.8 K; mixed metal nitrates co-precipitated by K ₂ CO ₃	Co ₂ O ₃ :Cr ₂ O ₃ :Al ₂ O ₃ =20:30:50 mixed metal nitrates co-precipitated by K ₂ CO ₃
Products, based on 100 wt. percent recovery:		
C ₂ -free gasoline, vol. percent.	94.5	93.3
Dry gas, wt. percent.	5.5	3.0
Coke, wt. percent.	0.8	1.5

¹ Charge: Oklahoma City naphtha; same charge as in Table IX except for the addition of thiophene to obtain a total sulfur content of 1.04 wt. percent, substantially all of which was thiophenic sulfur

These data show that the sulfur removal was greater than 90 per cent for both catalysts. The sulfur in the charge decreased the extent of aromatization in the same manner that is known to occur for other aromatization catalysts when used under similar conditions, such as molybdena-alumina. However, the liquid recovery was high and the coke formation low in both cases.

Although the present invention has been described in conjunction with certain embodiments, it is to be understood that modifications and variations therein may be made without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A process for effecting aromatization reforming of hydrocarbon mixtures containing aromatizable hydrocarbons, which comprises contacting said hydrocarbon mixtures with a chromium oxide-iron group metal oxide catalyst composition obtained by initially intimately mixing moist, undried hydrous chromium oxide with moist, undried hydrous iron group metal oxides in proportions such that the final chromium oxide-iron group metal oxide catalyst composition will contain chromium oxide and iron group metal oxide in a mol per cent ratio, expressed on the basis of the metal sesquioxides, varying between about 40:60 and about 70:30, respectively, to produce a mixture; treating said mixture at temperatures sufficient to dry the mixture but below about 350° C. to produce a dehydrated mixture; comminuting said dehydrated mixture; and calcining said dehydrated mixture at temperatures varying between about 500° C. and about 600° C., under non-oxidizing conditions and for a period of time of at least about five hours; at temperatures falling within the range varying between about 450° C. and about 650° C.; at hydrocarbon partial pressures falling within the range varying from atmospheric and up to about 30 pounds per square inch gauge; at liquid hourly space velocities falling within the range varying between about 0.2 and about 2.5; and under total pressures varying from atmospheric and up to about 300 pounds per square inch gauge.

2. A process for effecting aromatization reforming of hydrocarbon mixtures containing aromatizable hydrocarbons, which comprises contacting said hydrocarbon mixtures with a catalyst comprising a chromium oxide-iron group metal oxide composition obtained by initially

intimately mixing moist, undried hydrous chromium oxide with moist, undried hydrous iron group metal oxides in proportions such that the final chromium oxide-iron group metal oxide composition will contain chromium oxide and iron group metal oxide in a mol per cent ratio, expressed on the basis of the metal sesquioxides, varying between about 40:60 and about 70:30, respectively, to produce a mixture; treating said mixture at temperatures sufficient to dry the mixture but below about 350° C. to produce a dehydrated mixture; comminuting said dehydrated mixture at temperatures varying between about 500° C. and about 600° C., under non-oxidizing conditions and for a period of time of at least about five hours; alumina in amounts varying between about 30 mol per cent and about 95 mol per cent, based on the total oxides in the catalyst; and a promoter selected from the group consisting of potassium oxide and copper oxide, in amounts of at least about 0.2 per cent and up to about 5 per cent, by weight; at temperatures falling within the range varying between about 485° C. and about 550° C.; at hydrocarbon partial pressures falling within the range varying from atmospheric and up to about 30 pounds per square inch gauge; at liquid hourly space velocities falling within the range varying between about 0.5 and about 1.0; and under total pressures varying from atmospheric and up to about 30 pounds per square inch.

3. A process for effecting desulfurization and aromatization reforming of sulfur-bearing hydrocarbon mixtures containing aromatizable hydrocarbons, which comprises contacting said hydrocarbon mixtures with a catalyst comprising a chromium oxide-iron group metal oxide composition obtained by initially intimately mixing moist, undried hydrous chromium oxide with moist, undried hydrous iron group metal oxides in proportions such that the final chromium oxide-iron group metal oxide composition will contain chromium oxide and iron group metal oxide in a mol per cent ratio, expressed on the basis of the metal sesquioxides, varying between about 40:60 and about 70:30, respectively, to produce a mixture; treating said mixture at temperatures sufficient to dry the mixture but below about 350° C. to produce a dehydrated mixture; comminuting said dehydrated mixture; and calcining said dehydrated mixture at temperatures varying between about 500° C. and about 600° C., under non-oxidizing conditions and for a period of time of at least about five hours; alumina in amounts varying between about 30 mol per cent and about 95 mol per cent, based on the total oxides in the catalyst; and a promoter selected from the group consisting of potassium oxide and copper oxide, in amounts of at least about 0.2 per cent and up to about 5 per cent, by weight; at temperatures falling within the range varying between about 485° C. and about 550° C.; at hydrocarbon partial pressures falling within the range varying from atmospheric and up to about 30 pounds per square inch gauge; at liquid hourly space velocities falling within the range varying between about 0.2 and about 0.5; in the presence of hydrogen in mol

ratios of hydrogen to hydrocarbon varying between about 1:1 and about 5:1, respectively; and under total pressures varying between about 50 and about 150 pounds per square inch gauge.

4. A process for effecting aromatization reforming of hydrocarbon mixtures containing aromatizable hydrocarbons, which comprises contacting said hydrocarbon mixtures with a catalyst comprising a chromium oxide-iron group metal oxide composition obtained by initially intimately mixing moist, undried hydrous chromium oxide with moist, undried hydrous iron group metal oxides in proportions such that the final chromium oxide-iron group metal oxide composition will contain chromium oxide and iron group metal oxide in a mol per cent ratio, expressed on the basis of the metal sesquioxides, varying between about 40:60 and about 70:30, respectively, to produce a mixture; treating said mixture at temperatures sufficient to dry the mixture but below about 350° C. to produce a dehydrated mixture; comminuting said dehydrated mixture; and calcining said dehydrated mixture at temperatures varying between about 500° C. and about 600° C., under non-oxidizing conditions and for a period of time of at least about five hours; alumina in amounts varying between about 30 mol per cent and about 95 mol per cent, based on the total oxides in the catalyst; and a promoter selected from the group consisting of potassium oxide and copper oxide, in amounts of at least about 0.2 per cent and up to about 5 per cent by weight; at temperatures falling within the range varying between about 500° C. and about 600° C.; at hydrocarbon partial pressures falling within the range varying from atmospheric and up to about 30 pounds per square inch gauge; at liquid hourly space velocities falling within the range varying between about 0.5 and about 1.0; in the presence of steam in mol ratios of steam to hydrocarbon varying between about 1:2 and about 1:4, respectively; and under total pressures varying from atmospheric and up to about 30 pounds per square inch gauge.

WILLIAM H. LANG.
WILLIAM A. STOVER.
CARLOS L. GUTZEIT.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,486,781	Meigs	Mar. 11, 1924
2,184,235	Groll et al.	Dec. 19, 1939
2,203,826	Komarewsky	June 11, 1940
2,239,000	Groombridge	Apr. 22, 1941
2,337,191	Greensfelder et al.	Dec. 21, 1943
2,399,895	Segfried et al.	May 7, 1946
2,401,246	Hull	May 28, 1946
2,401,846	Sumerford	June 11, 1946
2,408,131	Voorhies	Sept. 24, 1946
2,408,140	Gutzeit	Sept. 24, 1946
2,474,213	Black	June 23, 1949
2,486,361	Nahin et al.	Oct. 25, 1949
2,487,564	Layng	Nov. 8, 1949

OTHER REFERENCES

Sergienko, Bull. acad. sci. URSS, Classe sci. chim., 1941, pages 177-190. Abstracted in Chemical Abstracts, vol. 37, col. 3064 (1943).