



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/06267 <b>(22) International Filing Date:</b> 28 July 1992 (28.07.92)  <b>(30) Priority data:</b> 738,369                      31 July 1991 (31.07.91)                      US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).  <b>(72) Inventors:</b> HAAG, Werner, Otto ; 38 Pine Knoll Drive, Lawrenceville, NJ 08648 (US). HARANDI, Mohsen, Nadimi ; 12 Catbird Court, Lawrenceville, NJ 08648 (US). OWEN, Hartley ; 5 Riverview Terrace, Belle Mead, NJ 08502 (US).		<b>(74) Agents:</b> PAULAN, Alverna, M. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).  <b>(81) Designated States:</b> AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> DEHYDROGENATION AND ISOMERIZATION/OLIGOMERIZATION OF LIGHT PARAFFIN FEEDS  <b>(57) Abstract</b>  The invention relates to a dual catalyst process for increasing the production of total olefin and iso-olefin derivatives in the conversion of alkane containing feeds.		

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DEHYDROGENATION AND ISOMERIZATION/OLIGOMERIZATION  
OF LIGHT PARAFFIN FEEDS

This invention relates to a dual catalyst process for increasing the production of the total olefin and iso-olefin derivatives in the conversion of alkane-containing feeds

The present invention provides a process for converting a  $C_4$ - $C_{10}$  paraffin-containing feed to effluents which contain substantially less paraffins comprising:

contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

wherein the alkane and alkene contain 4 to 10 carbon atoms and each of the alkane and the alkene are normal or branched chain;

contacting the product with an acidic catalyst composition comprising a zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof, under temperature conditions ranging from 260° to 649°C (500° to 1200°F); and,

decreasing the content of the normal alkenes in the product.

The present invention also provides a process for converting a  $C_4$ - $C_{10}$  paraffin-containing feed to effluents which contain substantially less paraffins comprising:

contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

wherein the alkane and alkene contain 4 to 10 carbon atoms; and each of the alkane and the alkene are normal or branched chain;

contacting the product with an acidic catalyst composition comprising a zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof, under olefin oligomerization/cracking/aromatization conditions including a WHSV of from 0.2 to 50, and at a temperature of from 232° to 649°C (450° to 1200°F), and the hydrocarbon partial pressure ranges between 0.5 to 40 atmospheres, and decreasing the content of the alkenes in the product.

The present invention further provides a process for converting a  $C_4$ - $C_{10}$  paraffin-containing feed to an effluent which is an aromatic  $C_5$ + product stream comprising:

contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

contacting the product with an acidic catalyst composition, under conditions effective to aromatize the product including a temperature ranging from 400° to 700°C, a pressure ranging from 0 to 1000 psig, hydrogen to hydrocarbon ratios from 0-20 and WHSV of 0.1 to 500, and an acidic catalyst comprising a zeolite or a metal impregnated zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof, and producing the aromatic C<sub>6</sub>+ product stream.

The four C<sub>4</sub> mono-olefins, 1-butene, cis-2-butene, trans-2-butene and 2-methylpropene, are collectively called butylenes. The term isobutylene is by established usage interchangeable with the nomenclature 2-methylpropene, while the other three isomers are n-butenes. Often they are treated collectively because the four mono-olefins are obtained as mixtures, from various processes. The C<sub>4</sub> olefins are often contained in mixtures of C<sub>1</sub>-C<sub>5</sub>'s, which include both alkanes and alkenes.

Isobutylene is a desirable reactant for the production of alkylate, an oligomer of petroleum refinery C<sub>3</sub>-C<sub>4</sub> off gases, which includes high octane gasoline components, and for the production of methyl-t-butyl ether, when isobutylene is reacted with methanol.

The drawing is a graph of the plot of the selectivity of the production to iso-olefin vs. conversion of n-butenes. The drawing illustrates the effect of catalyst on iso-butene selectivity, of 1-butene conversion at 450°C and one atmosphere.

The process of the invention comprises catalytic production of the C<sub>4</sub> olefin(s) from feeds containing C<sub>4</sub> alkanes which olefins are selected from the group consisting of 1-butene, cis-2-butene, and

trans-2-butene and contact of the  $C_4$  olefin(s) with a catalyst which will convert at least one of these butenes to an isobutylene product, optionally, relatively free of oligomers of any of the  $C_4$  monoolefins. The class of reactant feeds includes alkanes of  $C_4$ - $C_{10}$  carbon atoms including n-butane, n-pentane and n-hexane. Dehydrogenation of those respective alkane reactants will yield n-butene, n-pentene and n-hexene. The class of reactant feeds may come from catalytic cracking of a higher molecular weight paraffin feed, over a catalyst in the vapor phase. The  $C_4$  fraction may be separated from  $C_5^+$  hydrocarbons, which may also be effected, by conventional pressure distillation. However, this separation is not essential and is not necessarily preferred. Catalyst contact with the feed can be undertaken in a fixed bed, moving bed or fluidized system.

Catalytic production of the  $C_4$  olefin(s) including 1-butene, cis-2-butene, trans-2-butene and 2-methylpropene, is undertaken, under catalytic dehydrogenation conditions, in the presence of a non-acidic catalyst.

In this stage of the invention process, catalytic dehydrogenation comprises contacting a paraffin, with the dehydrogenation catalyst, preferably a non-acidic catalyst composition, to produce the corresponding unsaturated analog together with  $H_2$ . The catalytic dehydrogenation exhibits high selectivity with respect to production of the unsaturated analog, with substantially little, if any, selectivity for hydrogenolysis (cracking) and with substantially little, if any, selectivity for isomerization. In dehydrogenation the feed can comprise at least one

unsubstituted chain paraffinic compound in which the paraffinic moiety has four to ten carbon atoms. In accordance with the invention, dehydrogenation of the paraffinic moiety occurs to yield the unsaturated analog.

Preferred pressures for catalytic dehydrogenation range from 0.1 to 3 atmospheres. However, pressures up to 500 psig can be employed, particularly if a light olefin is co-fed for transhydrogenation. The catalytic dehydrogenation is conducted at elevated temperatures ranging from 400° to 700°C and, most preferably, from 400° to 600°C. Reactor inlet H<sub>2</sub>/feed ratios are 5 or less; even at reactor inlet ratios of zero (0), there will be a hydrogen partial pressure in the reactor because hydrogen is a by product of dehydrogenation. The liquid hourly space velocity of 0.1 to 50, preferably 0.5 to 10.

Under those conditions, in the presence of the dehydrogenation catalyst described below, the catalytic dehydrogenation of C<sub>4</sub> alkanes exhibits little, if any, selectivity for isomerization. Accordingly, the unsaturated product of this stage of the process invention can be characterized as substantially free (preferably less than 5%) of molecular products of less (fewer number) carbon atoms than the reactants and as substantially free of isomers of the reactant or of isomers of its unsaturated analogs of the reactant. This stage of the process can be conducted in the presence or absence of added hydrogen and in the presence or absence of diluents inert to conditions of the catalytic dehydrogenation such as steam, nitrogen, and methane. In particular, dehydrogenation can be advantageously conducted at low hydrogen partial pressure.



The dehydrogenation catalyst comprises a dehydrogenation metal and a non-acidic microporous crystalline material. The term "crystalline" used to refer to these materials relates to the ordered  
5 definite crystalline structure of the material which is unique and thus identifiable by a characteristic X-ray diffraction pattern.

The term "microporous", as it refers to such material, relates to pores or channels, with diameters  
10 of less than 20 Angstroms. Examples of these microporous crystalline materials include crystalline silicates, crystalline alumino-silicates (zeolites), crystalline ALPOs, crystalline SAPO and related compositions and intercalated pillared materials  
15 derived from clays, layered silicates and titanates. The crystalline silicate, alumino silicate (zeolites), ALPOs and SAPOs, have pores of uniform size and channel systems which are uniquely determined by unit structure of the material. The uniform pore size and/or channel  
20 systems allow such a material to selectively absorb molecules of certain dimensions and shapes. In the art, microporous material having pores or channels of less than 20 Angstroms, can be divided into small, medium and large pore by the diameters of those pores,  
25 or channels. The pores of the small pore material have an average diameter of less than 5 Angstroms; medium size pores range from an average diameter of 5 to 7 Angstroms, and large pore silicates indicates a diameter of greater than 7. The word "average" is used  
30 to refer to diameter to embrace those species in which the pore is elliptical. Alternatively, the demarcation between small, medium, and large pore materials can be based on the following sorption properties (measured at

room temperature for crystallites having a minimum dimension of 0.1 micron):

1. Small pore:  $n\text{-C}_6/\text{i-C}_6$  sorption ratio greater than approximately 10.

5 2. Medium pore:  $n\text{-C}_6/\text{i-C}_6$  is less than 10 and  $n\text{-C}_6/\text{Mesitylene}$  sorption ratio greater than approximately 5.

3. Large pore:  $n\text{-C}_6/\text{Mesitylene}$  sorption ratio less than approximately 5.

10 In the art, zeolites are a subclass of crystalline microporous silicates. Zeolites can contain aluminum as well as silicon. In some zeolites, the upper limit of the silicon/aluminum atomic ratio is unbounded. ZSM-5 is one such example wherein the silica/alumina  
15 mole ratio is at least 12 and up to infinity. By way of illustration, U.S. Patent No. 3,941,871, reissued as RE 29,948, discloses a porous crystalline silicate made from a reaction mixture containing no deliberately added aluminum and exhibiting the X-ray diffraction  
20 pattern characteristic of ZSM-5 zeolites; in certain examples tin is deliberately added to the silicate synthesis mixture.

Zeolites can be acidic or non-acidic, depending on the framework aluminum content and on the amount of  
25 compensating cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ , etc. ALPOs described in U.S. Patent No. 4,310,440 are neutral. SAPOs described, for example, in U.S. Patent No. 4,440,871, can be acidic or non-acidic depending on the ratio of framework Al:P therein and the compensating  
30 cation, such as  $\text{Na}^+$ ,  $\text{K}^+$  (other than proton species and other than proton forming species such as  $\text{NH}_4^+$ ).

The microporous crystalline materials of the non-acidic catalyst preferably contain a modifier which is tin, iridium, thallium, lead or iridium. The

modifier content of the crystalline microporous materials can range from 0.01 to 20 wt %. Practically, the modifier content will range from 0.1 to 10 wt %.

5 The crystalline microporous modifier containing materials of the invention are characterized by Si/Al ratios of at least 2. However, the silica:alumina ratio of the zeolite can be up to 1000, or greater. In a preferred embodiment, the aluminum content of these materials is less than 0.1 wt % and, more preferably,  
10 less than 0.02 wt %.

The crystalline microporous modifier containing material of the invention can contain other elements including boron, iron, chromium and gallium. The content of these other elements in the crystalline  
15 modifier containing silicates can range from 0 to 10 wt %.

The modifier containing crystalline materials of the invention described herein are crystalline in the sense that they are identifiable as isostructural with  
20 zeolites by X-ray powder diffraction pattern.

The crystalline microporous modifier containing material has an X-ray diffraction pattern which corresponds to a zeolite, SAPO, ALPO, etc.

In a preferred embodiment, the pore size of the microporous crystalline modifier-containing silicates  
25 ranges from 5 to 8 Angstroms. In a preferred embodiment, the microporous crystalline material containing modifier exhibits the structure of ZSM-5, by X-ray diffraction pattern. The X-ray diffraction  
30 pattern of ZSM-5 has been described in U.S. Patent No. 3,702,886 and RE 29,948.

The amount of dehydrogenation metal in the catalyst can range from 0.01 to 30 wt % and, preferably, 0.1 to 10 wt % of the crystalline modifier

containing material. In a preferred embodiment, platinum is the hydrogenation/ dehydrogenation metal. However, the hydrogenation/ dehydrogenation metal can be any Group VIII metal including those of the platinum group, chromium and vanadium.

The compositions comprising hydrogenation/ dehydrogenation metal combined with the crystalline modifier containing silicates do not exhibit any appreciable acid activity. These catalysts would meet the criteria of non-acidic catalysts described by Davis and Venuto, J. CATAL. Vol. 15, p.363 (1969).

When, as in embodiments herein, the crystalline modifier dehydrogenation metal containing material exhibits an X-ray diffraction pattern of a zeolite, at least some of the dehydrogenation metal may be intrazeolitic, that is, some of that metal is within the pore structure of the crystal, although some of that metal can be on the surface of the crystal. A test for determining whether, for example, Pt is intrazeolitic or extrazeolitic in the case of ZSM-5 is reported by R. M. Dessau, J. CATAL. Vol. 89, p. 520 (1984). The test is based on the selective hydrogenation of olefins.

Compositions of the invention used in catalysis decrease the hydrogen content of the reactant to produce a product having the same number of carbon atoms as the number of carbon atoms in the reactant. By comparison, modifier-free counterparts of those compositions catalyzed also hydrogenolysis of paraffins, e.g., to methane, as a major competing side reaction; and, accordingly, the latter compositions exhibit decreased selectivity for the aromatization of paraffins but increased selectivity for C<sub>1</sub>-C<sub>5</sub> paraffin production.

One way of incorporating modifier into the composition of this invention is by incorporation during the synthesis of the non-acidic crystalline microporous material. Alternatively, modifier can be incorporated with the crystalline composition post-synthesis of the microporous crystalline material. The dehydrogenating metal can be incorporated during or after synthesis of the microporous crystalline material. The dehydrogenating metal can be incorporated before, simultaneously with or after modifier incorporation.

Alternatively, reverse procedures can be applied in which the dehydrogenation function is first introduced with subsequent modifier incorporation. Stepwise preparation includes techniques of cocrystallization, impregnation, or exchange. Simultaneous incorporation includes the combination of modifier with the dehydrogenation/hydrogenation function during synthesis (i.e., crystallization) or simultaneously after synthesis of the crystalline material.

A modifier-free material can be treated with modifier compounds at elevated temperatures. Such treatments can be conducted so that the source of modifier is either in the gaseous or the liquid phase including the aqueous phase (such as modifier II). Alternatively, a modifier-free crystalline reactant can simply be impregnated with modifier source and then calcined at temperatures above 400°C.

The modifier-free catalyst can have high silica:alumina ratios or contain other elements such as boron, chromium, iron, and gallium. Silicates containing 0.1 wt % or less aluminum are preferred. In materials of the invention, all cation-exchangeable

5 sites are occupied by non-hydrogen (non-proton) and by  
non-hydrogen precursors, such as  $\text{NH}_4^+$ . Specifically,  
such sites are occupied by  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$  or admixtures  
thereof. The alkali metals serve to neutralize any  
acidity due to framework aluminum. The source of  
alkali metal cation can derive from cations  
incorporated during synthesis, in excess of the  
aluminum content thereof. Alternatively, one can treat  
the final product with a basic solution of an alkali  
10 metal hydroxide as a final step prior to use, as  
described, for example, in U.S. Patent No. 4,652,360.

15 In a preferred embodiment, the non-acidic  
crystalline microporous modifier containing silicates  
of the invention are treated with  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  in  
aqueous solution which has a pH of at least 7 to  
incorporate the necessary platinum for catalyst  
composition formulation.

20 The non-acidic, crystalline, microporous, modifier  
or iridium modifier and dehydrogenation metal  
containing materials of the invention can be combined  
with a matrix or binder material to render them  
attrition resistant and more resistant to the severity  
of the conditions to which they will be exposed during  
use in hydrocarbon conversion applications. The  
25 combined compositions can contain 1 to 99 wt % of the  
materials of the invention based on the combined weight  
of the matrix (binder) and material of the invention.  
When used in dehydrogenation and/or dehydrocyclization,  
the material of the invention will preferably be  
30 combined with non-acidic matrix or binder materials. A  
preferred matrix or binder material would be silica,  
when the materials of the invention are used in  
dehydrogenation/hydrogenation. However, the binder or  
matrix material can be inactive material and synthetic

or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides, e.g. alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the new composition, i.e. combined therewith, which is active, tends to alter the conversion and/or selectivity of the overall catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g. bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e. clays, oxides, etc., function as binders for the catalyst. It may be desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay binders have been employed normally only for the purpose of improving the crush strength of the overall catalyst.

Naturally occurring clays which can be composited with the new crystal include the montmorillonite and kaolin families which include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

Binders useful for compositing with the present crystal also include inorganic oxides, notably alumina. In addition to the foregoing materials, the crystalline tin material can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The relative proportions of finely divided crystalline material and inorganic oxide gel matrix vary widely, with the crystal content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 wt % of the composite.

Other dehydrogenation catalysts which can be employed are oxides of chromium, molybdenum, palladium, platinum, or admixtures thereof on alumina (e.g. gamma-or eta- alumina). C.F. Thomas, CATALYTIC PROCESSES AND PROVEN CATALYSTS, Academic Press, pp. 41-44,45 (1970).

In the presence of the non-acidic catalyst, the olefin content of the feed is increased. In the presence of the acidic catalyst, also employed in the process of the invention, the olefinic components of the feed are isomerized and/or converted to oligomers. In a preferred embodiment of this invention, a single reactor in which the concentration of the acidic catalyst in the reactor is at least 1 to 100 times less than the dehydrogenation catalyst concentration is used. The dehydrogenation non-acidic catalyst converts alkanes to olefins which undergo oligomerization and/or isomerization over the acidic catalyst which shifts alkane dehydrogenation equilibrium toward completion.



Hydrogenation of the oligomers, which consumes the  $H_2$  produced in the dehydrogenation reaction, also tends to shift the equilibrium to result in high conversion of alkanes to olefins. Both hydrogenation and  
5 oligomerization reactions are exothermic and therefore minimize the process heat input requirement. Furthermore, the oligomers can undergo aromatization to produce  $C_6^+$  aromatic rich effluent.

The acidic catalyst may be in the form of a  
10 powder, spheres, beads or extrudates. Supports, matrix and binder materials for the acidic catalyst can be those described above.

In one embodiment of this invention, the  $C_4$  olefins produced in the dehydrogenation reaction can be  
15 contacted with ZSM-35, in the acidic form, to increase the isobutylene content of the composition, and to decrease the content of the  $C_4$ s other than isobutylene, while maintaining the total  $C_4$  isomers substantially constant, without substantial oligomerization thereof.  
20 Accordingly, the product of the process of the invention is substantially free of oligomerization products of the any one of the  $C_4$  mono-olefins, when the acidic catalyst is ZSM-5, ZSM-23, ZSM-22, ZSM-34, ZSM-35, ZSM-48 and zeolites of similar structure and  
25 the proposed operating conditions are used.

ZSM-5 is described in U.S. Patent No. 3,702,886; ZSM-23 in U.S. Patent No. 4,076,842; ZSM-22 in U.S. Patent No. 4,556,477; ZSM-23 in U.S. Patent No. 4,076,842; ZSM-34 in U.S. Patent No. 4,086,186; ZSM-35  
30 in U.S. Patent No. 4,016,245; and, ZSM-48 in U.S. Patent No. 4,375,573.

The ZSM-23 containing catalyst may be unsupported or supported on a matrix or may be in the form of a

powder, spheres, beads or extrudates. Supports for the zeolites are described above.

5 Catalyst contact with the C<sub>4</sub> mono-olefin feed can be undertaken in a fixed bed, moving bed or fluidized bed. The physical conditions of the vapor phase catalysis includes a temperature within the range of from 427° to 621°C (800° to 1150°F), preferably from 538° to 593°C (1000 to 1100°F). The operating pressure is preferably equal or close to the dehydrogenation  
10 step. WHSV range from 10 to 1000, preferably from 50 to 150 for butene isomerization.

The conversion of n-butene to iso-butene over ZSM-23 at atmospheric pressure, high WHSV, and 538°C (1000°F) occurs with no significant oligomerization to  
15 heavier molecules. The ZSM-23 isomerization of n-butene(s) is favored by low reactant partial pressure and high operating temperature in the dehydrogenation process.

As a catalyst, the ZSM-5 can be used in olefin  
20 isomerization at essentially the same operating range as ZSM-23.

The isomerization catalyst may follow the dehydrogenation catalyst in a separate reactor or in the same reactor. It is preferred, however, to mix the  
25 two catalysts or provide the two components in a single binder. This can result in a higher conversion of n-paraffins, since the equilibrium is shifted by the isomerization reaction.

As a catalyst, the ZSM-5 can be used in olefin  
30 isomerization at temperatures between 427° and 593°C (800° and 1100°F), at weight hourly space velocities between 10 and 200.

The ZSM-5 containing catalyst can be used for olefin oligomerization under olefin oligomerization

conditions, e.g., at a temperature of 232° to 649°C (450° to 1200°F), preferably 288° to 482°C (550° to 900°F); and the hydrocarbon partial pressure ranges between 0.5 to 40 atmospheres, preferably between 1 and 20 atmospheres and a WHSV of from 0.2 to 50, preferably 0.5 to 10. As noted in U.S. Patent No. 4,021,502, the oligomerization feed can be pure C<sub>2</sub>-C<sub>5</sub> olefin, or it may be prepared by forming mixtures thereof and mixtures with C<sub>1</sub>-C<sub>5</sub>. As noted in U.S. Patent No. 4,021,502, the product of that oligomerization is a gasoline blending stock. Under the preferred conditions, the gasoline fraction contains predominantly higher olefins.

Alternatively, the acidic zeolite catalyst containing, for example, ZSM-5, can be used to aromatize the olefins produced as a result of the first stage of the process. Temperatures of aromatization range from 400° to 700°C, pressure ranging from 0 to 1000 psig, hydrogen to hydrocarbon ratios are from 0 to 20 and WHSV from 0.1 to 500. Preferred conditions are temperatures of from 400° to 650°C, atmospheric to 500 psig, absence of hydrogen and WHSV of from 0.5 to 10.

The foregoing condition relate to conditions for separate reactors containing separate catalyst beds. When mixed catalysts are employed and the dehydrogenation catalyst is admixed with the acidic catalyst, because of equilibrium shifts, the temperature conditions of dehydrogenation per se may be constructively reduced. In mixed catalyst systems, the temperature can range from 399° to 677°C (750° to 1250°F), preferably from 454° to 593°C (850° to 1100°F) at pressures ranging from 15 psia to 400 psia, preferably from 30-150 psia; WHSV for dehydrogenation can range from 1-100 preferably from 3-10; WHSV for

isomerization can range from 5-200, preferably from 10-30; WHSV for oligomerization (olefin interconversion) can range from 1-40, preferably from 3-8; and WHSV for aromatization can range from 0.5-20, preferably from 1-5.

#### EXAMPLES

The tin containing microporous crystalline materials can be formed as in Examples 1-6.

Example 1

Tin ZSM-5 silicate was synthesized in a static system at 149°C (300°F). 400 g 28.5% sodium silicate (Q-brand) was added to a solution of 60 g 50% tetramethylammonium chloride, 15 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 30 g 98%  $\text{H}_2\text{SO}_4$ , and 60g TPA+Br- in 2250 g water. The mixture was stirred and then placed in a polypropylene bottle in an autoclave for 5 days. The product was 85% crystalline ZSM-5 and consisted of large 5-10 micron crystals. In this and following preparations, the zeolitic silicates produced were characterized as having at least one crystal dimension which was at least 0.5 microns; it analyzed for 80.4%  $\text{SiO}_2$ , 0.30%  $\text{Al}_2\text{O}_3$ , 3.78% Sn, 2.00% Na, 7.70% C, and 1.05% N.

Example 2

Another tin containing ZSM-5 sample was synthesized by employing 0.69 g  $\text{Sn(II)SO}_4$  to form a hydrogel reaction mixture which is described by the following mole ratios:

$\text{SiO}_2/\text{Sn}$	$\text{H}_2\text{O}/\text{Sn}$	$\text{OH}^-/\text{SiO}_2$	$\text{Na}^+/\text{SiO}_2$	$\text{TPA}^+/\text{SiO}_2$
75	40	0.30	0.35	0.10

The hydrogel was reacted at 160°C for 5 days with stirring (400 rpm) before quenching. The resulting crystalline product was processed in the usual manner by filtering, washing, and drying. X-ray diffraction analysis of the product zeolite showed it to be 100% crystalline ZSM-5. SEM indicated an average crystal size greater than 2 microns.

Example 3

A tin containing ZSM-5 sample was synthesized in a similar manner except that the  $\text{SiO}_2/\text{Sn}$  ratio was 150 and the  $\text{Na}^+/\text{SiO}_2$  was 0.31. The crystalline ZSM-5 product contained 1.36% Sn, 0.0025% Al, 0.93% Na, and 89.31% Ash.

Example 4

A tin containing ZSM-5 sample was synthesized in a similar manner except that the  $\text{SiO}_2/\text{Sn}$  ratio was 50, the  $\text{Na}^+/\text{SiO}_2$  was 0.38, and the synthesis time was 4 days.

Example 5

A tin containing ZSM-5 sample was synthesized at a  $\text{SiO}_2/\text{Sn}$  ratio of 38, a  $\text{Na}^+/\text{SiO}_2$  ratio of 0.40, and a synthesis time of 3 days.

Tin incorporation was achieved during the zeolite synthesis, i.e., tin salts were added directly to the high silica ZSM-5 synthesis mixture. SEM data suggests that a significant portion of the tin is located outside of the large crystals formed (Figure 1). Nevertheless, some tin must be inside the ZSM-5 crystals, since it modifies the selectivity of the platinum, which itself is intracrystalline.

Platinum was incorporated by ion-exchange of the calcined zeolites, probably, via exchange for sodium ions associated with internal silyloxy groups. The presence of intracrystalline (intrazeolitic) platinum was confirmed by the extremely low benzene hydrogenation rates ( $\text{TON} = 4 \text{ min}^{-1}$  at  $100^\circ\text{C}$ ) measured for these catalysts.

Example 6

Platinum incorporation into the silicates of Examples 1-5 was undertaken. The as-synthesized tin silicates were calcined first in nitrogen and then in air at  $520^\circ\text{C}$ . The calcined materials were ion-exchanged with aqueous  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  at room temperature; typically, 15-20 mg per gram silicate was used in a non-acidic aqueous medium. The platinum tetramine-containing silicates were then calcined in oxygen to  $350^\circ\text{C}$  at  $0.5 \text{ C/min}$ .

Elemental analysis of the tin silicate of Example 3 after platinum incorporation indicated Pt=0.80%, Sn=1.54%, Al=31ppm.

5 Elemental analysis of the tin silicate of Example 1 after platinum incorporation, Pt=0.65%, Sn=3.50%, Al=0.093%.

Example 7

10 In Table 1, the results of passing 1-butene (152 Torr); over HZSM-23 ( $\alpha=19$ ) (.06013 grams) under the conditions set forth are set forth:

TABLE I

	Press (Psig)			
		3	5	8
	Temp (°C)	500	501	501
	Flow (CC/Min)	100	150	200
5	WHSV	-----	-----	-----
WEIGHT PERCENT IN PRODUCT STREAM				
	C1	0.238	0.177	0.146
	C2	0.031	0.022	0.018
	C2=	0.281	0.199	0.158
10	C3	0.014	0.008	0.006
	C3=	1.351	0.971	0.775
	I-C4	0.158	0.110	0.086
	N-C4	0.561	0.461	0.408
	1-C4=	16.516	17.915	19.113
15	I-C4=	34.474	30.874	27.636
	TR-2-C4=	26.935	28.726	30.140
	CIS-2-C4=	18.518	19.904	21.043
	N-C5	0.000	0.000	0.000
	3M-1-C4=	0.000	0.000	0.000
20	1-C5=	0.000	0.000	0.000
	TR-2-C5=	0.119	0.076	0.057
	CIS-2-C5=	0.044	0.025	0.000
	TERT-C5=	0.654	0.476	0.384
	C6=	0.079	0.055	0.029
25	C7+	0.026	0.000	0.000
	C1-C5 PARFNS	1.002	0.778	0.664
	C2=	0.281	0.199	0.158
	C3=	1.351	0.971	0.775
	C4=	96.443	97.419	97.932
30	C5=	0.817	0.577	0.441
	C6=	0.079	0.055	0.029
	C7+	0.026	0.000	0.000
	Conversion of N-C4=	38.031	33.455	29.704
35	I-C4=	34.474	30.874	27.636
	Selectivity to I-C4=	90.647	92.285	93.039



CLAIMS:

1. A process for converting a  $C_4-C_{10}$  paraffin-containing feed to effluents which contain substantially less paraffins comprising:

5       contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the  
10       modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

15       wherein the alkane and alkene contain 4 to 10 carbon atoms and each of the alkane and the alkene are normal or branched chain;

20       contacting the product with an acidic catalyst composition comprising a zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof, under temperature conditions ranging from 260° to 649°C (500° to 1200°F); and,

      decreasing the content of the normal alkenes in the product.

2. The process of Claim 1, wherein the alkane and the alkene each contain 4 carbon atoms.

3. The process of Claim 2, which further includes producing isobutylene.

4. The process of Claim 2, which further includes recovering oligomers of alkenes containing 4 carbon atoms.

5        5.    The process of Claim 1, wherein the acidic catalyst and the non-acidic catalyst are present in a relative concentration, in which relative concentration the acidic catalyst is at least 3 to 100 times less than the non-acidic catalyst.

      6.    The process of Claim 1, which further includes recovering oligomers of the alkene.

      7.    The process of Claim 1, wherein the crystalline material has a zeolite structure.

      8.    The process of Claim 1, wherein the dehydrogenation metal is a Group VIII metal.

      9.    The process of Claim 1, wherein the dehydrogenation metal is platinum.

      10.   The process of Claim 1, wherein the platinum is intrazeolitic.

      11.   The process of Claim 1, wherein the non-acidic catalyst contains up to 10 wt % tin.

      12.   The process of Claim 1, wherein at least some of the tin is intrazeolitic.

      13.   The process of Claim 1, wherein the crystalline material is isostructural with zeolite and contains cations of alkali metal or alkali earth metal in excess of the aluminum content of the zeolite.

      14.   The process of Claim 1 wherein the crystalline material is a silicate.

15. A process for converting a  $C_4-C_{10}$  paraffin-containing feed to effluents which contain substantially less paraffins comprising:

5       contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the  
10       modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

15       wherein the alkane and alkene contain 4 to 10 carbon atoms; and each of the alkane and the alkene are normal or branched chain;

20       contacting the product with an acidic catalyst composition comprising a zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof, under olefin oligomerization/cracking/aromatization conditions including a WHSV of from 0.2 to 50, and at a temperature of from 232° to 649°C (450° to 1200°F), and the hydrocarbon partial pressure ranges between 0.5 to 40 atmospheres, and decreasing the content of the alkenes in the product.

16. The process of Claim 15, which further includes recovering oligomers of the alkenes containing 4 carbon atoms.

5       17. The process of Claim 15, wherein the acidic catalyst and the non-acidic catalyst are present in a relative concentration, in which relative concentration the acidic catalyst is at least 1 to 100 times less than the non-acidic catalyst.

18. The process of Claim 15, wherein the crystalline material has a zeolite structure.

19. The process of Claim 15, wherein the conditions include pressures from 0.1 to 20 atmospheres; elevated temperatures ranging from 400° to 700°C; and a weight hourly space velocity of 0.1 to 50.

20. A process for converting a  $C_4-C_{10}$  paraffin-containing feed to an effluent which is an aromatic  $C_5+$  product stream comprising:

5       contacting the feed comprising an alkane under dehydrogenation conditions, with a non-acidic catalyst comprising a dehydrogenation metal in an amount from 0.01 to 20 wt %, and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, the  
10       modifier being present in an amount of from 0.01 to 20 wt % to produce a product in which the alkane has been converted to alkene;

15       contacting the product with an acidic catalyst composition, under conditions effective to aromatize the product including a temperature ranging from 400° to 700°C, a pressure ranging from 0 to 1000 psig, hydrogen to hydrocarbon ratios from 0-20 and WHSV of 0.1 to 500, and an acidic catalyst comprising a zeolite  
20       or a metal impregnated zeolite selected from ZSM-5, ZSM-23, ZSM-22, ZSM-35 and ZSM-48 and admixtures thereof; and

producing the aromatic  $C_6+$  product stream.

21. The process of Claim 20, wherein the alkane and the alkene each contain 4 carbon atoms.

22. The process of Claim 20, wherein the acidic catalyst and the non-acidic catalyst are present in a relative concentration, in which relative concentration the acidic catalyst is at least 1 to 100 times less  
5       than the non-acidic catalyst.

23. The process of Claim 20, wherein the material has a zeolite structure.

24. The process of Claim 20, wherein the dehydrogenation metal is a Group VIII metal.

25. The process of Claim 20, wherein the dehydrogenation metal is platinum.

26. The process of Claim 20, wherein the material is isostructural with zeolite and contains cations of alkali metal or alkali earth metal in excess of the aluminum content of the zeolite.

27. The process of Claim 26, wherein the dehydrogenation conditions include pressures from 0.1 to 30 atmospheres; elevated temperatures ranging from 400° to 700°C; and weight hourly space velocity of 0.1 to 50.

28. In a process for converting  $C_4$ - $C_{20}$  alkanes to  $C_5$ + boiling range product, the improvement comprising:

contacting the alkanes with a mixed catalyst system including (a) a non-acidic catalyst which comprises a dehydrogenation metal and a non-acidic microporous crystalline material containing a modifier selected from indium, thallium, lead, tin and iridium, wherein the amount of the metal ranges from 0.01 to 20 wt %, and the amount of modifier ranges from 0.01 to 20 wt %, and (b) an acidic zeolite, wherein the acidic zeolite is selected from ZSM-35, ZSM-22, ZSM-23, ZSM-5, and ZSM-48; and recovering  $C_5$ + boiling range product.

29. The process of Claim 28, wherein the acidic catalyst and the non-acidic catalyst are present in a relative concentration, in which relative concentration the acidic catalyst is at least 1 to 100 times less  
5 than the non-acidic catalyst and wherein the non-acidic catalyst contains metal and a binder wherein the amount of the metal ranges from 0.01 to 20 wt %, under conditions including a temperature ranging from 399° to 677°C (750° to 1250°F); a pressure ranging from 15 psia  
10 to 400 psia; and a WHSV for ranging from 1-100.

30. The process of Claim 28, wherein WHSV ranges from 1-40 and the C<sub>5</sub>+ product is highly olefinic and contains iso-olefins.

31. The process of Claim 28, wherein WHSV ranges from 1-5 and the C<sub>5</sub>+ product is highly aromatic.

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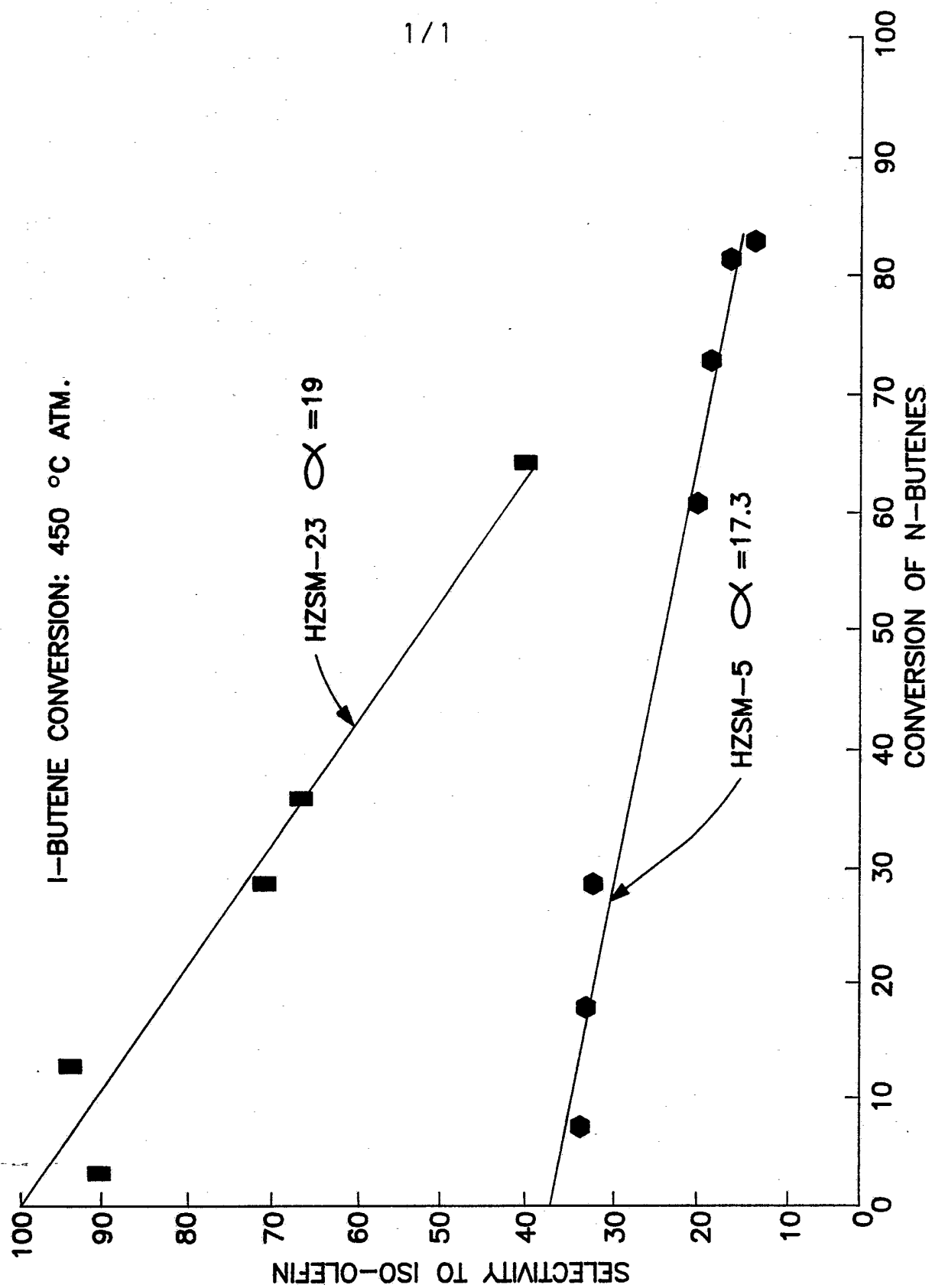


FIG. 1

SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/06267

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C10G 35/04, 35/06, 59/02

US CL :208/138, 64, 65

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/138, 64, 65; 585/664, 666

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: Dehydrogenation, non-acidic catalyst, indium, thallium, lead, tin, iridium, isomerization, acidic catalyst, ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,990,710 (DESSAU ET AL.) 05 FEBRUARY 1991. See col. 2, lines 66-68; col. 3, lines 1-3, 7-22, 45-58; col. 5, lines 14-18; col. 6, lines 2-4, 22-28, 57-62; col. 7, lines 20-29.	1-31
Y	US, A, 4,324,940 (DESSAU) 13 APRIL 1982. See col. 3, lines 53-66, col. 4, lines 24-28, 35-44.	1-31

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 SEPTEMBER 1992

Date of mailing of the international search report

16 OCT 1992

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