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DESCRIPTION

TECHNICAL FIELD

[0001] A catalyst for stationary and/or fluid bed dehydrogenation processes for hydrocarbons, which is particularly useful in vapor phase dehydrogenation to produce lower olefins, is described herein. Methods of making the catalyst are also described. One embodiment of the catalyst comprises an alumina carrier, with at least, chromium oxide, sodium oxide and potassium oxide. The resultant catalyst exhibits higher conversion and selectivity and high olefin yields after the catalyst ages, low deactivation rates and robust hydrothermal stability in comparison to prior art catalysts.

BACKGROUND ART

[0002] Supported metal oxide catalysts are used in a variety of commercial reactions, and are typically present in the form of pellets or other shaped products or powders having active metal sites on or within an essentially chemically inert carrier. In many catalytic processes, a chemical reactant contained in a gas stream is passed over or through a bed containing the catalyst. The reactant contacts the active site on the catalyst, a chemical conversion occurs to generate one or more products, and those products are released from the catalyst's active sites. For commercial operations, it is desirable that the gas stream be passed over the catalyst bed at an essentially constant and rapid rate.

[0003] In the production of olefins and diolefins by catalytic dehydrogenation, it is desirable to obtain as high a yield of the desired olefins or diolefins as possible with high conversion and selectivity during a single passage of the material to be catalyzed through the dehydrogenation zone. It is also important to produce as small an amount of by-products and coke during the dehydrogenation process as is possible. Further, long catalyst life and low deactivation rates are important.

[0004] Selectivity plays an important role in olefin production. As the annual production of olefins (such as isobutylene, propylene and butadiene) by catalytic dehydrogenation is at least 3 million tons, even relatively small increases in selectivity of the catalyst, as small as a fraction of a percentage point, can be very beneficial financially for olefin producers.

[0005] One of the most important of the dehydrogenation processes is the Houdry paraffin dehydrogenation process that is conducted in a cyclic reaction mode. Cyclic processes make use of parallel reactors that contain a shallow bed of a catalyst. The feed is preheated through a fixed heater before passing over the catalyst in the reactors. The hot product is then cooled, compressed and sent to the product fractionation and recovery station. To facilitate continuous operation, the parallel reactors are operated in staggered, timed cycles. Each complete cycle typically consists of dehydrogenation, regeneration, reduction and purge segments. In addition, to provide more favorable equilibrium conditions, the reactors are generally operated at sub-atmospheric pressures

during the dehydrogenation cycle. The regeneration cycle, operating in the range of 500 to 700°C, provides heat for the subsequent dehydrogenation reaction. Because of such high temperatures, the effective life of the dehydrogenation catalyst is generally no longer than about two to three years. After such periods of time on line, catalyst replacement is required because of reduced levels of conversion and selectivity. For instance, after two to three years of operation, the catalyst's conversion is generally reduced by 5 to 15% and its selectivity drops by about 5 to 20%. Thus, improvement in the catalyst's conversion and selectivity toward the end of a two to three year cycle can significantly improve the overall process efficiency.

[0006] While it is common to optimize a catalyst's performance based on its initial conversion and selectivity, it is also important to optimize catalyst performance based on its conversion and selectivity after aging.

[0007] Processes utilizing chromia-alumina catalysts for the conversion of paraffinic and olefinic hydrocarbons are well known and have been described in technical literature as well as in numerous patents starting in the 1940's. One typical composition for catalysts that are used for dehydrogenation of paraffins and olefins contains chromium oxide on the surface of an aluminum oxide carrier. Although chromia-alumina catalysts have a relatively high dehydrogenation activity, they often suffer from rapid coke formation during the dehydrogenation reaction. Consequently, frequent high temperature regeneration cycles are mandated. Because of these frequent regeneration cycles, it is required that the chromia-alumina catalyst have a high degree of hydrothermal stability in order to extend the life of the catalyst.

[0008] Other types of dehydrogenation catalysts contain platinum, palladium or other precious metals on various carriers, including alumina carriers. However, while both platinum-based and chromium-based dehydrogenation catalysts are used commercially, the nature and behavior of these two catalyst types are quite different.

[0009] For example, after regeneration, the small Pt particles on the surface of the platinum-based dehydrogenation catalysts become agglomerated, which causes a significant loss of activity. To return these catalysts to an active state, the Pt particles are subsequently re-dispersed by treatment with chloride. In contrast, chromium-based dehydrogenation catalysts require no such chloride treatment. In fact, chlorides are a severe poison for chromium-based dehydrogenation catalysts and must therefore be limited to no more than 1.0 ppmw in the form of HCl in the feed.

[0010] On the other hand, sulfur is a severe poison to platinum-based dehydrogenation catalysts, but chromium-based dehydrogenation catalysts can tolerate sulfur levels as high as 100 ppmw with little or no impact on performance.

[0011] These two types of dehydrogenation catalysts are also quite different from a compositional standpoint. In the case of platinum-based dehydrogenation catalysts, the active dehydrogenation component (Pt) is typically present in an amount of less than 1 wt%. In addition, these platinum-based catalysts require an element from Group IV as a promoter. They also typically contain a significant amount of a halogen (up to 1 wt%). In contrast, chromium-based dehydrogenation catalysts contain the active dehydrogenation component (Cr_2O_3) at higher percentage levels, typically 10-30 wt%, require no group IV element, and must not contain any halogen, as it is a

poison.

[0012] These two types of dehydrogenation catalysts are also quite different from an operational standpoint. Platinum-based dehydrogenation catalysts require the hydrocarbon feed to be diluted with hydrogen and/or steam while chromium-based dehydrogenation catalysts require no hydrogen dilution with the feed and water is a poison for the catalyst.

[0013] Accordingly, a person skilled in the art would not anticipate that a change in composition of a platinum-based dehydrogenation catalyst which resulted in improved performance would necessarily cause a similar improvement in performance for a chromium-based dehydrogenation catalyst.

[0014] Additional components are often added to dehydrogenation catalysts to enhance their reactivity or selectivity or to enhance the operating characteristics of the carrier. One common additive is a single alkali metal or alkaline earth metal. Numerous patents have described the addition of an alkali metal to dehydrogenation catalysts, wherein the alkali metal of choice generally includes any of the alkali metals from lithium to cesium. Sodium or potassium compounds are often chosen for use because of their low cost and simplicity of utilization. It has generally been assumed that there is no significant difference in performance of the catalysts regardless of the choice of the alkali metal promoter although some references have recommended one alkali metal over other alkali metals.

[0015] There have also been some disclosures of a combination of alkali metals being utilized for chromium-based dehydrogenation catalysts. For example, U.S. Patent No. 7,012,038 discloses a dehydrogenation catalyst which requires the addition of both lithium oxide and sodium oxide to a chromium oxide/alumina catalyst.

[0016] In addition, the use of lithium and potassium to a platinum-alumina dehydrogenation catalyst is disclosed in U.S. Patent No. 4,677,237.

[0017] Notwithstanding the prior art, additional improved chromia/alumina catalysts with enhanced conversion and selectivity, especially as the catalyst ages, are still needed.

[0018] US 2006/149112 relates to a multi-layered dehydrogenation catalyst system and process of use. WO 2005/040075 relates to a catalyst for dehydrogenation of hydrocarbons. WO 03/106388 relates to a paraffin dehydrogenation catalyst. US 5,378,350 relates to process and catalyst for dehydrogenation or dehydrocyclization of hydrocarbons.

DISCLOSURE OF EMBODIMENTS OF THE INVENTION

[0019] According an aspect of the present invention there is provided a catalyst for use in the dehydrogenation process as defined in Claim 1. The use of sodium oxide and potassium oxide together as promoters provides enhanced performance for these catalysts over prior art dehydrogenation catalysts, although this phenomenon primarily occurs after aging, wherein improvements in conversion and selectivity are particularly noted.

[0020] According to another aspect of the present invention there is provided a process for making a dehydrogenation catalyst as defined in Claim 11.

[0021] According to a further aspect of the present invention there is provided a process for dehydrogenation of a hydrocarbon composition as defined in Claim 14.

A. The Catalysts

[0022] The catalysts are intended for use in a stationary and/or fluid bed dehydrogenation process for converting dehydrogenatable hydrocarbons, for example C₂ - C₆ hydrocarbons, to olefins and/or diolefins. Dehydrogenation reactions are normally conducted at the highest practical throughput rates which produce an optimum yield. Yield is dependent upon conversion and selectivity of the catalyst. These characteristics determine the efficiency of the process. Selectivity of the catalyst is defined as the ratio of the number of moles of the desired product, e.g. propylene, isobutylene or higher molecular weight olefin produced, to the number of moles of paraffin converted. Activity or conversion refers to that portion of feedstock that is converted to both the desired products and by-products. For high efficiency of the process, it is important to have both a high initial yield with the fresh catalyst and high activity and selectivity of the catalyst as the catalyst ages. For purposes of this disclosure, a catalyst is considered "aged" after it has been utilized for about 7-8 months on stream. Alternatively, a catalyst is considered "aged" after it has been "artificially aged" in the manner discussed later. Both of these criteria (initial yield and yield after aging) are used to determine the catalyst's overall efficiency.

[0023] The dehydrogenation catalyst can be utilized in either a fluid bed or a stationary bed reactor.

[0024] As is known in the art, a supported metal oxide catalyst generally has one or more active metal oxides dispersed on, or compounded with, a carrier or support. Among other features, the support provides a means for increasing the surface area of the catalyst. Recommended carriers for the dehydrogenation catalysts include aluminum oxide, aluminas, such as gamma, eta, and theta alumina and the like or mixtures thereof, alumina monohydrate, aluminum trihydroxide, such as bayerite, nordstrandite, or gibbsite, or mixtures thereof, alumina-silica, transition aluminas, silica, silicates, zeolites and combinations thereof. The carrier comprised in the catalyst of the present invention is an alumina carrier, which can be selected from a group consisting of gamma-alumina, theta-alumina, eta-alumina, and combinations thereof. The carrier can be formed as a powder or in various shapes including, but not limited to, rings, spheres, cylinders, pellets, tablets, stars, tri-lobes, extrudates and the like. Commercial carriers of these types are well known in the industry.

[0025] For one type of dehydrogenation catalyst, chromium compounds are commonly used as the active phase because of its efficiency in paraffin dehydrogenation reactions. To persons skilled in the art, chromium-based dehydrogenation catalysts are not considered comparable to platinum and/or palladium-based dehydrogenation catalysts for the reasons previously discussed. Thus, in one embodiment, the catalyst does not contain platinum and/or palladium.

[0026] In many of the embodiments of the dehydrogenation catalysts described herein, the

chromium compound may be in the form of Cr_2O_3 . The chromium may be derived from CrO_3 or inorganic chromium salts, such as ammonium chromate or dichromate or chromium nitrate or other chromium salts or mixtures thereof. The chromium compound is converted to chromium oxide during one or more heating processes. The catalyst according to the present invention comprises from 10 wt% to 30 wt% chromium oxide based on the total catalyst weight. Although optionally, the catalyst may comprise from 15 wt% to 28 wt% chromium oxide, based on the total catalyst weight.

[0027] The introduction of the chromium compound into or on the support material can take place by any process well known in the art. Nonexclusive examples include, but are not limited to, simultaneous precipitation of aluminum oxide and chromium oxide from an aqueous solution containing aluminum and chromium salts, simultaneous impregnation on the carrier, treating an alumina support with a solution of chromic acid and mixing chromium oxide with aluminum hydroxide or oxide.

[0028] It has been surprisingly determined that the performance of a chromia/alumina catalyst can be significantly improved by the addition of the combination of sodium oxide with potassium oxide. In addition, it has surprisingly been discovered that the particular ratios that are chosen between the sodium oxide and potassium oxide enhance the performance of the catalyst.

[0029] It has also been surprisingly discovered that a chromia/alumina dehydrogenation catalyst containing a combination of both sodium oxide and potassium oxide substantially outperforms, especially after aging, chromia/alumina catalysts containing either, but not both of, sodium oxide and potassium oxide and also chromia/alumina catalysts that contain different combinations of alkali metals. Specifically, it has been surprisingly discovered that the performance of a chromia/alumina dehydrogenation catalyst to which have been added both sodium oxide and potassium oxide outperforms, especially after aging, a chromia/alumina catalyst which contains sodium oxide and lithium oxide, as taught by U.S. Patent No. 7,012,038. Thus, the alkali metal oxides added to the chromia/alumina dehydrogenation catalyst of the present invention consist of only sodium oxide and potassium oxide. Further, it has been surprisingly discovered that chromia/alumina dehydrogenation catalysts containing only sodium oxide and potassium oxide perform better than catalysts of a similar composition to which have been added additional alkali metals oxides, such as lithium oxide, especially after aging.

[0030] According to the present invention, the quantity of sodium oxide in the catalyst is from 0.1 to 2 wt.% based on the total weight of the catalyst, including the Na_2O . Optionally, the sodium oxide in the catalyst may be from 0.1 to 1wt.%, or from 0.1 to 0.3 wt% .

[0031] According to the present invention, the quantity of the potassium oxide is from 0.1 to 5 wt.% based on the total weight of the catalyst, including potassium oxide. Optionally the quantity of potassium oxide is from 0.1 to 2 wt. %, based on the total weight of the catalyst.

[0032] The weight ratio of the potassium oxide to sodium oxide in the catalyst may be from 0.1:1 to about 10:1 or alternatively 0.1:1 to 3:1, based on the total weight of the catalyst.

[0033] For catalyst use in a fluid bed, the catalyst may have a particle size of 20 μm to 150 μm . The carrier may be prepared by a variety of techniques that are known in the art. The carrier may be

spray-dried or pelletized and calcined at a temperature from about 500°C to about 1100°C.

[0034] Dehydrogenation catalysts containing chromia sometimes contain one or more additional promoters other than alkali metal oxides that are added to improve selected properties of the catalyst or to modify the catalyst activity and/or selectivity. Zirconium may be added to the catalyst as an additional promoter. The zirconium cation may be present in a variety of forms and from different zirconium sources, such as, ZrO_2 , zirconium hydroxide, a zirconium basic carbonate or a similar zirconium-containing compound or mixtures thereof. The zirconium compound, calculated as ZrO_2 , may comprise from about 0.1 wt% to about 15 wt%, based on the total catalyst weight, including the ZrO_2 . The catalyst may comprise from about 0.1 wt% to about 5 wt% zirconium compound. Alternatively the amount of the zirconium compound is from about 0.5 wt% to about 1.5 wt%. The zirconium compound, may be added to the catalyst in a variety of methods, as are known in the art, for example the zirconium may be co-impregnated with the chromium.

[0035] Magnesium may also be added to this catalyst as an additional promoter. The magnesium compound, calculated as magnesium oxide, comprises from about 0.1 to about 15 weight percent, based on the total catalyst weight, including the magnesium oxide. Optionally, the catalyst may comprise from about 0.1 to about 2 weight percent magnesium compound, or may comprise from about 0.5 to about 1 weight percent. The magnesium compound, may be added to the catalyst in a variety of methods, as are known in the art. The magnesium may, for example, be co-impregnated with chromium.

[0036] One example of a catalyst for use in dehydrogenation processes as described above comprises an alumina carrier; chromium oxide, at a concentration from 10 wt% to 30 wt% chromium oxide, based on the total catalyst weight, including the chromium oxide; sodium oxide, as a promoter, at a concentration from 0.1 wt% to 2 wt% sodium oxide based on the total catalyst weight, including the sodium oxide; potassium oxide, as a promoter, at a concentration from 0.1 wt% to 5 wt% potassium oxide, based on the total catalyst weight, including the potassium oxide; and from 0.1 to 15 wt% of zirconium oxide, based on the total catalyst weight.

[0037] Another example of a catalyst for use in dehydrogenation processes comprises an alumina carrier; chromium oxide, at a concentration from 10 wt% to 30 wt% chromium oxide, based on the total catalyst weight, including the chromium oxide; sodium oxide, as a promoter, at a concentration from 0.1 wt% to 2 wt% sodium oxide based on the total catalyst weight, including the sodium oxide; potassium oxide, as a promoter, at a concentration from 0.1 wt% to 5 wt% potassium oxide, based on the total catalyst weight, including the potassium oxide; and from 0.1 to 15 wt% of zirconium oxide, based on the total catalyst weight, and from 0.1 to 15 wt% of magnesium oxide, based on the total catalyst weight.

[0038] Yet another example of a catalyst for use in dehydrogenation processes comprises an alumina carrier; chromium oxide, at a concentration from 10 wt% to 30 wt% chromium oxide, based on the total catalyst weight, including the chromium oxide; and alkali metal oxides consisting of sodium oxide, as a promoter, at a concentration from 0.1 wt% to 2 wt% sodium oxide, based on the total catalyst weight, including the sodium oxide, and potassium oxide, as a promoter, at a concentration from 0.1 wt% to 5 wt% potassium oxide, based on the total catalyst weight, including the potassium oxide.

[0039] A further example of a catalyst for use in dehydrogenation processes comprises an alumina carrier; chromium oxide, at a concentration from 10 wt% to 30 wt% chromium oxide, based on the total catalyst weight, including the chromium oxide; alkali metal oxides consisting of sodium oxide, as a promoter, at a concentration from 0.1 wt% to 2 wt% sodium oxide, based on the total catalyst weight, including the sodium oxide, and potassium oxide, as a promoter, at a concentration from 0.1 wt% to 5 wt% potassium oxide, based on the total catalyst weight, including the potassium oxide; and zirconium oxide, as a promoter, at a concentration from 0.1 to 15 wt% zirconium oxide, based on the total catalyst weight, including the zirconium oxide.

B . Processes for making the catalysts

[0040] In one process for production of the catalyst, alumina pellets are prepared from aluminum trihydroxide, such as bayerite, gibbsite, nordstrandite or mixtures thereof, or other such alumina hydrates and aqueous nitric acid. The calcined alumina carrier may be in the form of gamma-, theta-, or eta-alumina and the like or mixtures thereof. The ingredients may be admixed for a mixing time providing completion of the reaction of the nitric acid with the alumina. The mixture is then formed into an intermediate precursor in an appropriate form and shaped, as required. For example, the mixture may be extruded through die plates to form strands that are cut into pellets. Alternatively, the alumina can be formed into other shapes including, but not limited to spheres, tablets, cylinders, stars, trilobes and the like.

[0041] The obtained pellets, if used, are then dried and heat treated at appropriate temperatures for a period sufficient to develop an attrition resistant structure with a surface area from about 15 to about 350 m²/g. These pellets, with or without adjustment of their surface area, may then be impregnated, with a solution of chromic acid with dissolved sodium and potassium compounds and, if desired, zirconium compounds, such as zirconium carbonate, and magnesium compounds, such as magnesium oxide. These additional components are added under conditions that produce a good distribution of the promoters on the carrier. The impregnated pellets are then dried at a temperature from about 90°C to about 180°C and calcined at a temperature from about 500°C to about 1100°C followed by a conditioning treatment in steam and air to fix the structure and initial activity of the catalyst.

[0042] Alternatively, the dehydrogenation catalyst may be prepared by mixing the alumina and the potassium, sodium and chromium compounds and other promoters, if desired, to form the end product followed by heat treatment at a temperature from about 500 to about 1,100°C, which is then followed by additional treatments as needed to fix the structure and activity of the catalyst.

[0043] An example of a process for making a dehydrogenation catalyst as described above, comprises mixing and shaping an alumina compound to form a shaped carrier; combining the shaped carrier with compounds comprising a chromium compound and alkali metal compounds, consisting essentially of a sodium compound and a potassium compound, to form a precursor material; and heating the precursor material to form the dehydrogenation catalyst.

C . Industrial applicability

[0044] The catalysts are intended for use in stationary and/or fluid bed dehydrogenation processes. The catalysts are effective as dehydrogenation catalysts and are especially effective in promoting the dehydrogenation of propane, isobutane, n-butane and isopentane to produce the related olefins or diolefins. The composition of the catalysts and the processing condition may be varied without exceeding the scope of the various embodiments of the invention.

[0045] Thermodynamically beneficial conditions for this paraffin dehydrogenation reaction are 400-700°C, for example 540-640°C, and at lower than atmospheric pressure, for example 0.2-0.5 atmosphere (20,265-50,662 Pascal) . The contact time of the reactant-containing gas with the catalyst is expressed in terms of liquid-hourly-space velocity (LHSV), which is defined as the volume of liquid hydrocarbon reactant per volume of catalyst per hour. The LHSV of the reactant can vary between 0.1 hour⁻¹ and about 5 hour⁻¹.

[0046] To predict catalyst stability over time, any suitable method can be used to age the catalyst, as is known in the art. Examples are long term tests in a small-scale adiabatic reactor at typical commercial operating conditions or placement of samples in baskets which are then loaded in a commercial reactor. Alternatively, a method of accelerating catalyst aging has been developed which is disclosed in "A New Houdry Catalyst for the 'Third Wave' Propane Dehydrogenation", M. A. Urbancic, V. Fridman, A. Rokicki North American Catalysis Society Meeting, Philadelphia, 2005, Paper 0-266.

[0047] To evaluate the stability of the catalysts, besides performance tests, the physical-chemical properties of the aged catalysts, such as alpha-(Cr,Al)₂O₃ phase content, and surface area are determined. As a reduction of surface area and the appearance of alpha-(Cr,Al)₂O₃ in catalysts occur as a result of aging, they can be used as indirect indicators of catalyst stability. Thus, lower alpha-(Cr,Al)₂O₃ content and/or higher surface area in the aged catalysts indicates higher stability of the catalysts.

D . Examples

[0048] The following examples illustrate and explain the various embodiments of the invention, but are not to be taken as limiting the embodiments in any regard. Parts and percentages are by weight unless otherwise designated.

Comparative Example 1

[0049] A dehydrogenation catalyst, with a composition of 19.7 wt.% Cr₂O₃ and 0.65 wt.% Na₂O with the remaining part comprising alumina is prepared as follows:

Hard alumina pellets are prepared from aluminum trihydroxide and aqueous nitric acid. The ingredients are thoroughly admixed; the mixing time provides time for completion of the reaction of nitric acid with the alumina. The mixture is then formed into pellets of 1/8" diameter (0.3175 cm).

The pellets are dried. The carrier is heat treated at 371°C in an atmosphere of air and then heat-treated at 616°C in air.

[0050] The aluminum oxide pellets are then impregnated with a solution of 42% by weight chromic acid and 1.1% sodium oxide to produce the weight percentages for the components listed above. The impregnated aluminum oxide is dried ten hours at 121°C and calcined at 760°C in 20 mol percent steam.

Inventive Example 2

[0051] The catalyst is prepared from the hard alumina pellets according to the process of Example 1. The hard alumina pellets are impregnated with a 42% by wt. solution of chromic acid, 0.4% by wt. sodium oxide and 1.1% by wt. potassium oxide to produce the weight percentages for the components that are listed below. The impregnated alumina pellets are dried ten hours at 121°C and calcined at 760°C according to the process of Example 1. The final formulation of the catalyst is 19.7 wt. % Cr_2O_3 , 0.21 wt. % Na_2O , 0.52 wt. % K_2O , with the remaining portion being Al_2O_3 .

Comparative Example 3

[0052] The catalyst of is prepared from hard alumina pellets according to the process of Example 1. The hard alumina pellets are impregnated with a 42% by wt. solution of chromic acid and 1.8% by wt. potassium oxide to produce the weight percentages for the components that are listed below. The impregnated alumina pellets are dried several hours at 121°C and calcined at 760°C according to Example 1. The final composition of the catalyst is 19.7 wt. % Cr_2O_3 and 0.93 wt. % K_2O , with the remaining portion being Al_2O_3 .

Comparative Example 4

[0053] The catalyst is prepared from hard alumina pellets according to the process of Example 1. The hard alumina pellets are impregnated with a solution of a mixture of a 42% by wt. solution of chromic acid, 0.95% by wt. sodium oxide, and 0.55% by wt. lithium oxide to produce the weight percentages for the components listed below. The impregnated alumina pellets are dried at 121°C and calcined at 760°C according to the process of Example 1. The final formulation of the catalyst is 19.5 wt. % Cr_2O_3 , 0.5 wt% Na_2O , 0.3 wt% Li_2O , with the remaining portion being Al_2O_3 .

Comparative Example 5

[0054] The catalyst is prepared from hard alumina pellets according to the process of Example 1. The hard alumina pellets are impregnated with a solution of a mixture of a 42% by wt. solution of chromic acid, 0.75% by wt. sodium oxide, and 0.25% by wt. lithium oxide, and 0.44% of potassium

oxide to produce the weight percentages for the components listed below. The impregnated alumina pellets are dried at 121°C and calcined at 760°C according to the process of Comparative Example 1. The final formulation of the catalyst is 19.8 wt. % Cr₂O₃, 0.45 wt % Na₂O, 0.21 wt% K₂O, 0.11 wt% Li₂O, with the remaining portion being Al₂O₃.

[0055] The catalysts of Comparative Examples 1, 3, 4, 5 and Inventive Example 2 are artificially aged at the conditions described above. The fresh and aged samples are then evaluated for catalyst performance after aging to the equivalent of 7-8 months on stream in order to determine their stabilities.

[0056] Tests for isobutane dehydrogenation performance are conducted in an externally heated tubular reactor of 1 inch (2.54 cm) internal diameter. Isobutane is introduced to the catalysts at controlled throughput and pressure (LHSV =1.0 and pressure = 0.33 atm. (33437 Pa.)) over a range of temperatures. Dehydrogenation products are analyzed to determine conversion of isobutane and isobutene selectivity. To test the performance of the catalysts "after aging", the catalysts were artificially aged using the procedures disclosed in "A New Houdry Catalyst for the Third Wave", disclosed above.

[0057] Table 1 shows the effect of the addition of both potassium oxide and sodium oxide as promoters on the performance of the catalysts according to the various embodiments of the invention.

Table 1

Composition and performance of the catalysts, fresh and after aging								
Example	Cr ₂ O ₃ % [wt]	Na ₂ O % [wt]	K ₂ O % [wt]	Li ₂ O % [wt]	Fresh Catalysts Performance at 1000°F		Aged Catalysts Performance	
					Isobutane conversion at 1000°F	Isobutylene Selectivity	Isobutane conversion at 1050°F	Isobutylene Selectivity at 60% conversion
Comparative Example 1	19.7	0.65	0	0	55.3	91.7	30.5	79.6
Inventive Example 2	19.7	0.21	0.5	0	55.6	91.5	48.1	87.6
Comparative Example 3	19.7	0	0.9	0	55.8	91.9	46.7	79.6
Comparative Example 4	19.5	0.5	0	0.3	55.9	92.1	42.6	80.2
Comparative Example 5	19.8	0.45	0.2	0.11	56.1	91.7	23.6	81.4

[0058] As shown in Table 1, after aging both the conversion and selectivity of the catalyst of Inventive Example 2 showed enhanced isobutane conversion and isobutylene selectivity over the catalysts of the Comparative Examples. This was a surprising result as the quantity of alkali metals present in Inventive Example 2 was similar to or less than the quantity of the alkali metals present in

each of the Comparative Examples. Further, the performance of the Inventive Example 2 catalyst was especially surprising in comparison to the performance of Comparative Example 4, which used the composition disclosed in U.S. Patent No. 7,012,038. Interestingly, the performance of the catalyst was not enhanced, and was in fact reduced when Li_2O was additionally added to a catalyst already containing Na_2O and K_2O . This was an especially surprising result.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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P a t e n t k r a v

- 5 **1.** Katalysator til anvendelse ved dehydrogeneringsprocesser omfattende:
en aluminabærer; chromoxid, i en koncentration fra 10 vægt-% til 30 vægt-%
chromoxid beregnet på basis af den samlede katalysatorvægt; natriumoxid,
som en promotor, i en koncentration fra 0,1 vægt-% til 2 vægt-% natriumoxid
beregnet på basis af den samlede katalysatorvægt; og kaliumoxid, som en
promotor, i en koncentration fra 0,1 vægt-% til 5 vægt-% kaliumoxid beregnet
10 på basis af den samlede katalysatorvægt; i hvilken natriumoxidet og kalium-
oxidet er de eneste alkaliske metaloxider.
- 15 **2.** Katalysator ifølge krav 1, hvor aluminabæreren er udvalgt fra en gruppe be-
stående af gamma-alumina, theta-alumina, eta-alumina og kombinationer
deraf.
3. Katalysator ifølge krav 1, hvor bæreren har en partikelstørrelse på fra 20 µm
til 150 µm.
- 20 **4.** Katalysator ifølge krav 1, hvor chromoxidet er til stede i en koncentration fra
15 vægt-% til 28 vægt-% beregnet på basis af den samlede katalysatorvægt.
- 25 **5.** Katalysator ifølge krav 1, hvor natriumoxidet er til stede i en koncentration
på fra 0,1 vægt-% til 1 vægt-% natriumoxid beregnet på basis af den samlede
katalysatorvægt.
- 30 **6.** Katalysator ifølge krav 1, hvor natriumoxidet er til stede i en koncentration
på 0,1 vægt-% til 0,3 vægt-% natriumoxid beregnet på basis af den samlede
katalysatorvægt.
- 7.** Katalysator ifølge krav 1, hvor kaliumoxidpromotoren er til stede i en kon-
centration på fra 0,1 vægt-% til 2 vægt-% kaliumoxid beregnet på basis af den
samlede katalysatorvægt.

8. Katalysator ifølge krav 1, hvor forholdet mellem kaliumoxid og natriumoxid er fra 0,1:1 til 10:1 beregnet på vægtbasis.
- 5 9. Katalysator ifølge krav 1, hvor forholdet mellem kaliumoxid og natriumoxid er fra 0,1:1 til 3:1 beregnet på vægtbasis.
- 10 10. Katalysator ifølge krav 1 yderligere omfattende mindst en yderligere promotor udvalgt fra gruppen bestående af zirkonium- og magnesiumforbindelser og blandinger deraf.
- 15 11. Fremgangsmåde til fremstilling af en dehydrogeneringskatalysator ifølge krav 1, omfattende at blande alumina med forbindelser omfattende chromforbindelser og alkaliske metalforbindelser, bestående af natrium- og kaliumforbindelser, for at danne et prækursormateriale, og at varmebehandle prækursormaterialet for at danne dehydrogeneringskatalysatoren.
- 20 12. Fremgangsmåde ifølge krav 11, hvor chrom tilsættes i form af en CrO_3 -opløsning, som imprægneres på aluminabæreren.
- 25 13. Katalysator ifølge krav 11, hvor natrium- og kaliumpromotorerne er co-imprægneret på bæreren sammen med chromet.
14. Fremgangsmåde til dehydrogenering af en carbonhydridsammensætning omfattende at føre carbonhydridsammensætningen hen over dehydrogeneringskatalysatoren ifølge krav 1.