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Iron oxide-based catalyst, its preparation and its use in a dehydrogenation process

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(54) Title: IRON OXIDE-BASED CATALYST, ITS PREPARATION AND ITS USE IN A DEHYDROGENATION PROCESS

(57) Abstract: A catalyst which is based upon an iron oxide and a compound of a lanthanide, of which iron oxide at least a portion is made by a process which involves heat decomposition of an iron halide, the lanthanide being in a quantity in the range of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as Fe<sub>2</sub>O<sub>3</sub>; a process for the preparation of the catalyst; a process for the dehydrogenation of an alkylaromatic compound which process involves contacting a feed containing the alkylaromatic compound with the catalyst; and a method of using an alkylaromatic compound for making polymers or copolymers, in which method the alkylaromatic compound has been prepared by the dehydrogenation process.

IRON OXIDE-BASED CATALYST, ITS PREPARATION AND ITS USE IN A DEHYDROGENATION  
PROCESS

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Field of the Invention

The present invention relates to an iron oxide based catalyst and to a process for the preparation of the catalyst. The present invention also relates to a process for the dehydrogenation of an alkylaromatic compound which process comprises contacting a feed comprising the alkylaromatic compound with the catalyst of this invention.

15 Background of the Invention

Iron oxide based catalysts are used in the dehydrogenation of an alkylaromatic compound to yield, as the desired, main product, the corresponding alkenylaromatic compound.

20 However, when using the iron oxide based catalysts in the dehydrogenation of alkylaromatic compounds, several side reactions occur which decrease the yield of alkenylaromatic compound and therefore effect the economy of the process unfavourably. One such side reaction is the formation of coke on the catalyst, which reduces the lifetime of the catalyst. Other side reactions involve the formation of an alkynylaromatic compound, a methylaromatic compound, and a de-alkylated aromatic compound. For example, in the dehydrogenation of ethylbenzene, the desired, main product is styrene and undesired byproducts are coke, phenylacetylene, toluene and benzene.

In view of the applicability and use of the alkenylaromatic compound, the alkynylaromatic compound is

frequently at least partly removed from the product of the dehydrogenation. This removal generally requires a separate process step, typically involving hydrogenation to the alkenylaromatic compound, using a selective  
5 hydrogenation catalyst.

US-A-5190906 and EP-A-1027928 disclose that the source of the iron oxide for use in the iron oxide catalysts may be a process which comprises heat  
10 decomposition of an iron halide. By nature, such iron oxide catalysts produced by heat decomposition of an iron halide contain residual iron halide.

For example, dehydrogenation catalysts are in commercial use for the dehydrogenation of an alkylaromatic compound, which catalysts are based on an  
15 iron oxide made by heat decomposition of an iron halide, and further contain a small amount of a lanthanide, for example 0.066 mole per mole of iron oxide, calculated as  $\text{Fe}_2\text{O}_3$ .

When in the dehydrogenation of an alkylaromatic  
20 compound such commercially available catalysts are applied alkynylaromatic compound is co-produced. It would be highly desirable to decrease the selectivity to the co-produced alkynylaromatic compound. As used herein, the selectivity to a particular compound means  
25 the fraction of the converted alkylaromatic compound yielding the particular compound.

#### Summary of the Invention

When using a catalyst which is based on an iron oxide obtained from iron halide heat decomposition and  
30 which contain halide by nature the selectivity to the alkynylaromatic compound is reduced, if the catalyst comprises, as described herein, a defined quantity of a lanthanide.

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This result is non-obvious, as a similar presence of a lanthanide in catalysts which are based on an iron oxide of another source does not significantly cause the selectivity to alkynylaromatic compound to decrease. The prior art documents acknowledged hereinbefore are silent as regards the particular influence of the lanthanide on the selectivity to alkynylaromatic compounds, which apparently depends on the iron oxide in respect of its source and/or the presence of halide.

Accordingly, to a first aspect of the present invention provides a catalyst which is based upon an iron oxide and a compound of a lanthanide, of which iron oxide at least a portion is made by a process which comprises heat decomposition of an iron halide, and which catalyst comprises the lanthanide in a quantity of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as  $\text{Fe}_2\text{O}_3$ , and has a median pore diameter of at most 5000Å.

In a second aspect, the present invention also provides a catalyst which is based upon an iron oxide and a compound of a lanthanide, of which iron oxide at least a portion has a residual halide content, and which catalyst comprises the lanthanide in a quantity of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as  $\text{Fe}_2\text{O}_3$ , and has a median pore diameter of at most 5000Å. In this embodiment, the residual halide content is in particular in the range of from 10 to 3000 parts per million by weight (ppmw), more in particular from 50 to 2000 ppmw, calculated as the weight of halogen relative to the weight of the said portion of the iron oxide.

In a third aspect, the present invention also provides a process for the preparation of a catalyst having a median pore diameter of at most 5000Å and comprising iron oxide and a lanthanide in a quantity of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as  $\text{Fe}_2\text{O}_3$ ,

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which process comprises preparing a mixture comprising an iron oxide and a compound of the lanthanide, and calcining the mixture, wherein at least a portion of the iron oxide is made by a process which comprises heat decomposition of an iron halide.

In a fourth aspect, the present invention further provides a process for the preparation of a catalyst having a median pore diameter of at most 5000Å and comprising iron oxide and a lanthanide in a quantity of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as Fe<sub>2</sub>O<sub>3</sub>, which process comprises preparing a mixture comprising an iron oxide and a compound of the lanthanide, and calcining the mixture, wherein at least a portion of the iron oxide has a residual halide content, in particular in the range of from 10 to 3000 ppmw, more in particular from 50 to 2000 ppmw, calculated as the weight of halogen relative to the weight of the said portion of the iron oxide.

According to a further aspect, the present invention provides a process for the dehydrogenation of an alkylaromatic compound which process comprises contacting a feed comprising the alkylaromatic compound with a catalyst according to the first or second aspect of this invention.

According to yet another aspect, the present invention provides a method of using an alkenylaromatic compound for making polymers or copolymers, comprising preparing an alkenyl aromatic compound using a process according to the third or fourth aspects of the invention; and polymerising said alkenylaromatic compound to form a polymer or copolymer.

#### Detailed Description of Embodiments of the Invention

As used herein, unless defined otherwise, the quantity of metal components in the catalysts and precursor mixtures, other than the iron components, is expressed as the number

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of moles of the metal relative to the total number of moles of iron oxide present in the catalyst, calculated as  $Fe_2O_3$ .

In some embodiments, the catalysts of this invention are based upon iron oxide which is obtained by heat decomposition of an iron halide, optionally applying an oxidising atmosphere wherein iron (II) is oxidised to iron (III). The halide may comprise a chloride and/or a bromide. Typically, the iron halide comprises iron dichloride, in particular iron trichloride. Heat decomposition may comprise spray roasting wherein an iron halide solution is sprayed from nozzles into a directly heated reaction chamber, as disclosed in US-A-5911967, which is herein incorporated by reference. Alternative heat decomposition methods utilise the iron halide as a gas or as a solid. Typically, the iron halide solution is a so-called waste pickle liquor. The iron oxide which is obtained by heat decomposition of the iron halide product may or may not be further treated, to decrease the iron halide content, before it is used in the present invention. Suitable treating methods are disclosed in US-A-5401485 and US-A-5597547, which are incorporated herein by reference.

In some embodiments the iron oxide obtained by heat decomposition of an iron halide has a residual halide content of less than 3000 ppmw, more typically less than 2000 ppmw, in particular less than 1500 ppmw, calculated as the weight of halogen relative to the weight of the iron oxide. Generally, it is preferred that the residual halide content is low. On the other hand, the residual halide may frequently be above 10 ppmw, more frequently above 50 ppmw, calculated

as the weight of halogen relative to the weight of the iron oxide.

A preferred catalyst can be obtained by combining yellow iron oxide with the iron oxide which is  
5 obtained by heat decomposition of an iron halide. The skilled person is aware that yellow iron oxide is a hydrated iron oxide, frequently depicted as  $\alpha$ -FeOOH or  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The yellow iron oxide may suitably be applied in a quantity of up to 50 %w, calculated as the weight of  
10  $\text{Fe}_2\text{O}_3$  relative to the total weight of iron oxide, as  $\text{Fe}_2\text{O}_3$ , present in the catalyst. Preferably, the yellow iron oxide is applied in a quantity of at least 1 %w, in particular from 5 to 30 %w, on the same basis, for example, 8.8 %w, 10 %w, 15 %w, 17 %w or 20 %w.

15 Minor amounts of other iron oxides or iron oxide-providing compounds may be combined with the iron oxide which is obtained by heat decomposition of an iron halide, but that is generally not preferred. Examples of such other iron oxides are black and red iron oxides. An  
20 example of a red iron oxide is so-called Penniman red iron oxide, i.e. iron oxide made by the Penniman method, for example as disclosed in US-A-1368748. Examples of iron oxide-providing compounds include goethite, hematite, magnetite, maghemite, lepidocrocite and  
25 mixtures thereof.

Generally, it is preferred that the quantity of the iron oxide which is obtained by heat decomposition of an iron halide is at least 50 %w, particular at least 70 %w, up to 100 %w, calculated as  $\text{Fe}_2\text{O}_3$  relative to the  
30 total weight of iron oxide, as  $\text{Fe}_2\text{O}_3$ , present in the catalyst.

The lanthanide is typically a lanthanide of atomic number in the range of from 57 to 66 (inclusive).

Preferably the lanthanide is lanthanum or, in particular, cerium. The lanthanide is typically applied in a quantity of at least 0.08 mole, in particular at least 0.1 mole, per mole iron oxide. The lanthanide is typically applied in a total quantity of at most 0.15 mole, more typically at most 0.14 mole, per mole iron oxide, as this tends to improve the overall selectivity to the desired alkenylaromatic compound. For example, the lanthanide may be applied in a quantity of 0.09 mole, or 0.113 mole, or 0.116 mole, or 0.12 mole, or 0.122 mole, or 0.123 mole, or 0.126 mole, or 0.15 mole, per mole iron oxide.

Typically, one or more compounds of molybdenum, tungsten, vanadium, copper and/or chromium may be present in the catalyst, as an additional component. Compounds of these metals tend to increase the dehydrogenation activity of the catalyst. In preferred embodiments tungsten or, in particular, molybdenum may be applied. The total quantity of one or more of molybdenum, tungsten, vanadium, copper and chromium may typically be at least 0.001 mole, more typically at least 0.005 mole, per mole iron oxide. Typically the total quantity is at most 0.1 mole, more typically at most 0.05 mol, in particular at most 0.02 mol, per mole iron oxide. For example, tungsten may be applied in a quantity of 0.0075 mole, or 0.0135 mole, or 0.0275 mole, per mole iron oxide; molybdenum may be applied in a quantity of 0.011 mole, or 0.018 mole, or 0.019 mole, per mole iron oxide; chromium may be applied in a quantity of 0.0085 mole, or 0.035 mole, per mole iron oxide; vanadium may be applied in a quantity of 0.01 mole, or 0.043 mole, or 0.045 mole, or 0.046 mole, or 0.047 mole, per mole

iron oxide; and copper may be applied in a quantity of 0.006 mole, or 0.081 mole, per mole iron oxide.

Typically, one or more compounds of an alkali metal may be present in the catalyst, as an additional component. Compounds of these metals tend to diminish the deposition of coke on the catalyst during the dehydrogenation, and thereby tend to increase the lifetime of the catalyst. They also tend to increase the selectivity to the desired alkenylaromatic compound. In preferred embodiments, the alkali metal is cesium or rubidium, or, in particular, potassium. The alkali metals may be applied typically in a total quantity of at least 0.2 mole, more typically at least 0.25 mole, in particular at least 0.3 mole, more in particular at least 0.45 mole, most in particular at least 0.55 mole, per mole iron oxide, and typically in a quantity of at most 5 mole, more typically at most 1 mole, per mole iron oxide. For example, the alkali metals may be applied in a total quantity of 0.525 mole, 0.534 mole, or 0.575 mole, or 0.615 mole, or 0.623 mole, or 0.629 mole, or 0.643 mole, or 0.85 mole, per mole iron oxide.

Typically, one or more compounds of an alkaline earth metal may be present in the catalyst, as an additional component. Compounds of these metals tend to increase the selectivity to the desired alkenylaromatic compound, and to decrease the rate of decline of the catalyst activity. In preferred embodiments, the alkaline earth metal is magnesium or, in particular, calcium. The alkaline earth metals may be applied typically in a quantity of at least 0.01 mole, more typically at least 0.02 mole, in particular at least 0.03 mole, per mole of iron oxide, and typically in a total quantity of at most 1 mole, more typically at most

0.2 mole, in particular at most 0.13 mole, more in particular at most 0.1 mole, per mole of iron oxide. For example, the alkaline earth metals may be applied in a total quantity of 0.025 mole, or 0.026 mole, or  
5 0.075 mole, or 0.076 mole, or 0.078 mole, or 0.079 mole, or 0.138 mole, or 0.14 mole, per mole of iron oxide.

It is not material to the invention which kind of lanthanide, molybdenum, tungsten, chromium, copper, vanadium, alkali metal or alkaline earth metal compounds  
10 are applied. Suitably, these metal compounds may, independently, be selected from hydroxides; bicarbonates; carbonates; carboxylates, for example formates, acetates, oxalates and citrates; nitrates; oxides; molybdates; tungstates; chromates; and vanadates. Oxygenated  
15 compounds like molybdates; tungstates; chromates; and vanadates may be employed as the acid, or as a suitable salt, such as the potassium, calcium, magnesium or any ammonium salt. The carboxylates are typically derived from carboxylic acids having up to 10 carbon atoms,  
20 inclusive, more typically from 1 to 6 carbon atoms, inclusive. More in general, after the calcination the metal compounds are typically present in the catalysts as the corresponding metal oxides and it is therefore preferred that the metal compounds applied are suitable  
25 metal oxide precursors.

The methods by which the catalysts may be prepared are not material to the invention. Typically, the catalyst may be prepared by preparing a mixture of the iron oxide(s) and any further component(s), such as  
30 any metal compound referred to above, in a sufficient quantity and calcining the mixture. Sufficient quantities may be calculated from the composition of the catalyst to be prepared. Examples of applicable methods

can be found in US-A-5689023, US-A-5171914, US-A-5190906, US-B1-6191065, and EP-A-1027928, which are herein incorporated by reference.

Before calcination, the mixture may be shaped  
5 into pellets of any suitable form, such as tablets, spheres, pills, saddles, trilobes, tetralobes, rings, stars, and hollow and solid cylinders. The addition of a suitable quantity of water, for example up to 30 %w, typically from 2 to 20 %w, calculated on the weight of  
10 the mixture, may facilitate the shaping into pellets. If water is added, it may be removed at least partly prior to calcination. Suitable shaping methods are pelletising, extrusion, pressing, spraying and spray drying. If desired, spray drying may be extended to  
15 include the calcination.

A shaping aid, or extrusion aid, may be applied, for example a saturated or unsaturated fatty acid (such as palmitic acid, stearic acid or oleic acid) or a salt thereof, a polysaccharide derived acid or a  
20 salt thereof, or graphite, starch, or cellulose. Any salt of a fatty acid or polysaccharide derived acid may be applied, for example an ammonium salt or a salt of any metal mentioned hereinbefore. The fatty acid may comprise from 6 to 30 carbon atoms (inclusive),  
25 preferably from 10 to 25 carbon atoms (inclusive). When a fatty acid or a polysaccharide derived acid is used, it may combine with a metal salt applied in preparing the catalyst, to form a salt of the fatty acid or polysaccharide derived acid. A suitable quantity of the  
30 shaping or extrusion aid is, for example, up to 1 %w, in particular 0.001 to 0.5%w, relative to the weight of the mixture to be shaped.

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The calcination comprises heating the mixture, typically in an inert or oxidising atmosphere, for example in nitrogen, helium, or an oxygen containing gas, such as air, oxygen enriched air or an oxygen/inert gas mixture. The calcination temperature is typically at least 600 °C, preferably at least 700 °C. It has been found that when the calcination is carried out at a higher temperature, the catalyst exhibits, advantageously, an increased selectivity to the formation of alkenylaromatic compound. When practicing embodiments of the process of the present invention, the calcination temperature will suitably be at most 1200 °C, more suitably at most 1100 °C. For example, the calcination may be carried out at 725 °C, or 767 °C, or 845 °C, or 860 °C, or 921 °C, or 925 °C, or 950 °C. Typically the duration of calcination is from 5 minutes to 12 hours, more typically from 10 minutes to 6 hours, for example 15 minutes, or 1.5 hours, or 3 hours, or 5 hours.

The surface structure of the catalyst, typically in terms of pore volume, median pore diameter and surface area, may be chosen within wide limits. The skilled person is aware that he can influence the surface structure by the selection of the temperature and time of calcination, and by the application of an extrusion aid.

Suitably, the pore volume is at least 0.01 ml/g, more suitably at least 0.05 ml/g. Suitably, the pore volume is at most 0.5, preferably less than 0.2, in particular at most 0.18 ml/g, more in particular at most 0.16 ml/g. For example, the pore volume may be 0.118 ml/g, or 0.122 ml/g, or 0.143 ml/g. The median pore diameter is at most 5000 Å, in particular less than 3000 Å. Suitably, the median pore diameter is at least 500 Å, in particular at least 1000 Å. In a

preferred embodiment, the median pore diameter is in the range of from 1200 to 2800 Å. For example, the median pore diameter may be 1360 Å, or 2080 Å, or 2670 Å. As used herein, the pore volumes and median pore diameters  
5 are as measured by mercury intrusion according to ASTM D4282-92, to an absolute pressure of 6000 psia ( $4.2 \times 10^7$  Pa using a Micromeritics Autopore 9420 model ( $130^\circ$  contact angle, mercury with a surface tension of 0.473 N/m). As used herein, median pore diameter is defined as the pore  
10 diameter at which 50 % of the mercury intrusion volume is reached.

The surface area of the catalyst is suitably in the range of from 0.01 to 20  $\text{m}^2/\text{g}$ , more suitably from 0.1 to 10  $\text{m}^2/\text{g}$ , for example 2.6  $\text{m}^2/\text{g}$ , or 3.4  $\text{m}^2/\text{g}$ , or 4.9  $\text{m}^2/\text{g}$ ,  
15 or 5  $\text{m}^2/\text{g}$ . As used herein, surface area is understood to refer to the surface area as determined by the BET (Brunauer, Emmett and Teller) method as described in Journal of the American Chemical Society 60 (1938) pp. 309-316.

20 The crush strength of the catalyst is suitably at least 10 N/mm, and more suitably it is in the range of from 20 to 100 N/mm, for example about 55 or 60 N/mm.

The present process for preparing an alkenylaromatic compound (hereinafter referred to as "the  
25 dehydrogenation process") comprises contacting the feed comprising the alkylaromatic compound with the catalyst of this invention. The dehydrogenation process is frequently a gas phase process, wherein a gaseous feed comprising the reactants is contacted with the solid  
30 catalyst. The catalyst is suitably present in the form of a fluidised bed of catalyst particles, or, more suitable, in the form of a packed bed. The process may be carried out as a batch process. However, it is more

suitable to carry out the dehydrogenation process as a continuous process. The skilled person will appreciate that hydrogen is a further product of the dehydrogenation process, and that the dehydrogenation in question is a  
5 non-oxidative dehydrogenation. Examples of applicable methods for carrying out the dehydrogenation process can be found in US-A-5689023, US-A-5171914, US-A-5190906, US-B1-6191065, and EP-A-1027928, which are herein incorporated by reference.

10 The alkylaromatic compound is typically an alkyl substituted benzene, although other aromatic compounds may be applied as well, such as an alkyl substituted naphthalene, anthracene or pyridine. The alkyl substituent may have any carbon number of two and  
15 more, for example, up to 6, inclusive. Suitable alkyl substituents are propyl ( $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 2-propyl (i.e. 1-methylethyl,  $-\text{CH}(\text{CH}_3)_2$ ), butyl ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 2-methyl-propyl ( $-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ ), and hexyl ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), in particular ethyl ( $-\text{CH}_2-\text{CH}_3$ ).  
20 Examples of suitable alkylaromatic compounds are butylbenzene, hexylbenzene, (2-methylpropyl)benzene, (1-methylethyl)benzene (i.e. cumene), 1-ethyl-2-methylbenzene, 1,4-diethylbenzene, in particular ethylbenzene.

It is advantageous to apply water, preferably  
25 in the form of steam, as an additional component of the feed. The presence of water will decrease the rate of deposition of coke on the catalyst during the dehydrogenation process. Typically the molar ratio of water to the alkylaromatic compound in the feed is in the  
30 range of from 1 to 50, more typically from 3 to 30, for example 5 or 10.

The dehydrogenation process is typically carried out at a temperature in the range of from 500 to

700 °C, more typically from 550 to 650 °C, for example  
600 °C, or 630 °C. In an embodiment, the dehydrogenation  
process is carried out isothermally. In other  
embodiments, the dehydrogenation process is carried out  
5 in an adiabatic manner, in which case the temperatures  
mentioned are reactor inlet temperatures, and as the  
dehydrogenation progresses the temperature may decrease  
typically by up to 150 °C, more typically by from 10 to  
120 °C. The absolute pressure is typically in the range  
10 of from 10 to 300 kPa, more typically from 20 to 200 kPa,  
for example 50 kPa, or 120 kPa.

If desired, one, two or more reactors, for  
example three or four, may be applied. The reactors may  
be operated in series or parallel. They may or may not  
15 be operated independently from each other, and each  
reactor may be operated under the same conditions or  
under different conditions.

When operating the dehydrogenation process as a  
gas phase process using a packed bed reactor, the LHSV  
20 may preferably be in the range of from 0.01 to  
10 l/(l.h), more preferably in the range of from 0.1 to  
2 l/(l.h). As used herein, the term "LHSV" stands for  
the Liquid Hourly Space Velocity, which is the liquid  
volumetric flow rate of the hydrocarbon feed, measured at  
25 normal conditions (i.e. 0 °C and 1 bar absolute), divided  
by the volume of the catalyst bed, or by the total volume  
of the catalyst beds if there are two or more catalyst  
beds.

In preferred embodiments the conditions of the  
30 dehydrogenation process are selected such that the  
conversion of the alkylaromatic compound is in the range  
of from 30 to 80 mole-%, more preferably in the range of

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from 35 to 75 mole-%, for example 40 mole-%, or 67 mole-%.

The alkenylaromatic compound may be recovered from the product of the dehydrogenation process by any known means. For example, the dehydrogenation process may include a fractional distillation or reactive distillation. If desirable, the dehydrogenation process may include a hydrogenation step in which at least a portion of the product is subjected to hydrogenation by which at least a portion of the alkenylaromatic compound, if any is present, is converted into the alkenylaromatic compound. The portion of the product subjected to hydrogenation may be a portion of the product which is enriched in the alkenylaromatic compound. Such hydrogenation is known in the art. For example, the methods known from US-A-5504268, US-A-5156816 and US-A-4822936, which are incorporated herein by reference, are readily applicable to some embodiments of the process of the present invention.

It is an unexpected benefit so some embodiments of the process of the present invention that the quantity of alkenylaromatic compound present in the dehydrogenation product, if any, is lower than without practicing the process of the invention, so that there is less need to apply the hydrogenation step, or the hydrogenation step may be carried out with less catalyst relative to the feed, or under milder conditions. It is also an unexpected benefit of some processes according to of the invention that an improved activity for a given selectivity or an improved selectivity for a given activity is obtained in the dehydrogenation, in particular when the alkali metal is employed at a relatively high quantity, for example at least 0.45 mole, in particular at least 0.55 mole, per mole iron oxide, preferably in combination with a high quantity of the

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lanthanide, for example at least 0.07 mole, in particular at least 0.1 mole, per mole iron oxide. Such catalysts tend to provide, in addition, an improved stability when operated in a dehydrogenation process wherein the molar ratio of water to the alkyaromatic compound is low, for example below 10, in particular at most 7.

The alkenylaromatic compound produced by the dehydrogenation process of this invention may be used as a monomer in polymerization processes and copolymerisation processes. For example, the styrene obtained may be used in the production of polystyrene, styrene/diene rubbers and the like. The improved catalyst performance achieved by catalysts in some embodiments of this invention leads to a more attractive process for the production of the alkenylaromatic compound and concurrently to a more attractive process which comprises producing the alkenylaromatic compound and the subsequent use of the obtained alkenylaromatic compound in the manufacture of polymers and copolymers which comprise monomer units of the alkenylaromatic compound. For applicable polymerization catalysts, polymerization processes, polymer processing methods and uses of the resulting polymers, reference is made to H F Marks, et al. (Ed.), "Encyclopedia of Polymer Science and Engineering", 2nd Edition, New York, Volume 16, pp. 1-246, and the references cited therein, which is/are incorporated herein by reference.

Embodiments of the invention will be illustrated by means of the following, non-limiting examples.

Example 1

A paste was made by mixing the following ingredients: iron oxide made by heat decomposition of an iron halide (Hoogovens Regenerated iron oxide, type RIO-

250), yellow iron oxide (Bayer, type 920Z), cerium carbonate, potassium carbonate, molybdenum trioxide, calcium carbonate, and water (about 10 %w, relative to the weight of the dry mixture). The paste was extruded  
5 to form 3-mm diameter cylinders cut into 6-mm lengths. The pellets were dried in air at 170 °C for 15 hours and subsequently calcined in air at 825 °C for 1 hours. After calcination, the composition of the catalyst was, per mole iron oxide, 0.615 mole potassium, 0.12 mole cerium,  
10 0.0175 mole molybdenum, 0.025 mole calcium, all per mole of iron oxide, as Fe<sub>2</sub>O<sub>3</sub>, present. The quantity of yellow iron oxide was 8.8 %, as Fe<sub>2</sub>O<sub>3</sub>, relative to the total quantity (number of moles) of iron oxide, as Fe<sub>2</sub>O<sub>3</sub>, present in the catalyst.

15 Three samples of the catalyst were used for the preparation of styrene from ethylbenzene under isothermal testing conditions in a reactor designed for continuous operation. The samples were used in three separate tests. In each test the conditions were as follows:  
20 absolute pressure 76 kPa, steam to ethylbenzene molar ratio 10, LHSV 0.65 l/l.h. In each test stable conditions were reached after 400 hours, and the temperatures were selected such that in each test a 70 %mole conversion of ethylbenzene was achieved. In the  
25 three tests, the temperatures were 584.4 °C, 582.6 °C, and 584.6 °C, i.e. on average 583.9 °C. The selectivity to styrene was on average 94.4 %mole.

Three samples of the catalyst were used for the preparation of styrene from ethylbenzene in three  
30 separate tests, as described in the previous paragraph, with the differences that the steam to ethylbenzene molar ratio 5, instead of 10, and the absolute pressure was lowered from 76 kPa to 40 kPa. In the three tests, the

temperatures were 596.8 °C, 597.4 °C, and 596.8 °C, i.e. on average 597.0 °C. The selectivity to styrene was on average 96.2 %mole.

Example 2

5                   A first experimental design was set-up and executed in accordance with the experimental procedures as described in Example 1. The experimental design covered variations in the quantities of

- potassium: 0.515, 0.565 and 0.615 mole/mole Fe<sub>2</sub>O<sub>3</sub>,
- 10 - calcium: 0.025, 0.050 and 0.075 mole/mole Fe<sub>2</sub>O<sub>3</sub>,
- cerium: 0.050, 0.085 and 0.120 mole/mole Fe<sub>2</sub>O<sub>3</sub>,
- molybdenum: 0.005, 0.0175 and 0.030 mole/mole Fe<sub>2</sub>O<sub>3</sub>,
- copper: 0, 0.050 and 0.100 mole/mole Fe<sub>2</sub>O<sub>3</sub>,
- chromium: 0, 0.050 and 0.100 mole/mole Fe<sub>2</sub>O<sub>3</sub>, and
- 15 - yellow iron oxide: 0, 10 and 20 %w, relative to the total quantity of iron oxide; and in
- the calcination temperature: 725, 825 and 925 °C.

The effects on the preparation of styrene from ethylbenzene were examined.

20                   It was found that an increase of the quantity of cerium provides a significant decrease of the selectivity to phenylacetylene.

                  Confirmation of this result was found by setting-up and executing a second experimental design

25 which differed from the first in that molybdenum was present in a fixed quantity of 0.0175 mole/mole Fe<sub>2</sub>O<sub>3</sub>, and that no copper and chromium were present.

                  For comparative purposes, a similar experimental design was set-up and executed, wherein a

30 Penniman red iron oxide was used instead of iron oxide made by heat decomposition of an iron halide. This experimental design covered variations in the quantities of

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- calcium: 0.025, 0.075 and 0.125 mole/mole  $\text{Fe}_2\text{O}_3$ ,
- cerium: 0.050, 0.075 and 0.100 mole/mole  $\text{Fe}_2\text{O}_3$ , and
- molybdenum : 0.010, 0.030 and 0.050 mole/mole  $\text{Fe}_2\text{O}_3$ .

The quantity of potassium was 0.550 mole/mole  $\text{Fe}_2\text{O}_3$ , no  
5 copper and chromium were present and the calcination  
temperature was 825 °C. It was found that an increase of the  
quantity of cerium does not provide a significant decrease  
of the selectivity to phenylacetylene.

The reference in this specification to any prior  
10 publication (or information derived from it), or to any  
matter which is known, is not, and should not be taken as an  
acknowledgment or admission or any form of suggestion that  
that prior publication (or information derived from it) or  
known matter forms part of the common general knowledge in  
15 the field of endeavour to which this specification relates.

Throughout this specification and the claims which  
follow, unless the context requires otherwise, the word  
"comprise", and variations such as "comprises" and  
"comprising", will be understood to imply the inclusion of a  
20 stated integer or step or group of integers or steps but not  
the exclusion of any other integer or step or group of  
integers or steps.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A catalyst which is based upon an iron oxide and a compound of a lanthanide, of which iron oxide at least a  
5 portion is made by a process which comprises heat decomposition of an iron halide, and which catalyst comprises the lanthanide in a quantity in the range of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated as  $\text{Fe}_2\text{O}_3$ , and has a median pore diameter  
10 of at most 5000 Å.
2. A catalyst as claimed in claim 1, wherein the iron oxide made by a process which comprises heat decomposition of an iron halide has a halide content of from 10 to 3000 parts per million by weight.
- 15 3. A catalyst which is based upon an iron oxide and a compound of a lanthanide, of which iron oxide at least a portion has a residual halide content, and which catalyst comprises the lanthanide in a quantity of from 0.07 to 0.15 mole per mole iron oxide present in the catalyst, calculated  
20 as  $\text{Fe}_2\text{O}_3$ , and has a median pore diameter of at most 5000 Å.
4. A catalyst as claimed in claim 3, wherein the residual halide content is in the range of from 10 to 3000 parts per million by weight, calculated as the weight of halogen relative to the weight of the portion of the iron  
25 oxide having a residual halide content.
5. A catalyst as claimed in any one of claims 1-4, wherein the lanthanide comprises cerium.
6. A catalyst as claimed in any one of claims 1-5, wherein the catalyst is further based upon a compound of an  
30 alkali metal, which catalyst comprises the alkali metal in a total quantity of at least 0.45 mole per mole iron oxide present in the catalyst, calculated as  $\text{Fe}_2\text{O}_3$ , in particular



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calcining the mixture.

14. A process as claimed in claim 13, wherein the temperature of calcination is in the range of from 600 to 1200 °C.

5 15. A process for the dehydrogenation of an alkylaromatic compound which process comprises contacting a feed comprising the alkylaromatic compound with a catalyst as claimed in any one of claims 1-12.

10 16. A process as claimed in claim 15, wherein the process is operated in the presence of water at a molar ratio of water to the alkylaromatic compound of below 10.

17. A process as claimed in claim 15 or 16, wherein the alkylaromatic compound comprises ethylbenzene.

15 18. A process for the preparation of polymers or copolymers comprising the steps of:  
- preparing an alkenylaromatic compound by employing a process according to any one of claims 15 to 17; and  
- polymerising said alkenylaromatic compound to form a polymer or copolymer.

20 19. A process according to any one of claims 13, 15 and 18 substantially as hereinbefore described with reference to the drawings and/or examples.