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(54) Title: CATALYTIC COMPOSITION FOR THE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

(57) **Abrégé/Abstract:**

Process for the catalytic dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane which comprises: A) dehydrogenating the hydrocarbon stream, optionally mixed with an inert gas, in a fluid bed reactor in the presence of a catalytic composition based on gallium and manganese supported on alumina modified with silica, at a temperature ranging from 400 to 700°C, at a total pressure ranging from 0.1 to 3 ata and with a GHSV (Gas Hourly Space Velocity) ranging from 50 to 10,000 h⁻¹; and B) regenerating and heating the catalyst, by means of the catalytic oxidation of a fuel, in a fluid bed regenerator at a temperature higher than 400°C.

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(54) Title: CATALYTIC COMPOSITION FOR THE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

(57) Abstract: Process for the catalytic dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane which comprises: A) dehydrogenating the hydrocarbon stream, optionally mixed with an inert gas, in a fluid bed reactor in the presence of a catalytic composition based on gallium and manganese supported on alumina modified with silica, at a temperature ranging from 400 to 700°C, at a total pressure ranging from 0.1 to 3 ata and with a GHSV (Gas Hourly Space Velocity) ranging from 50 to 10,000 h⁻¹; and B) regenerating and heating the catalyst, by means of the catalytic oxidation of a fuel, in a fluid bed regenerator at a temperature higher than 400°C.



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CATALYTIC COMPOSITION FOR THE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

The present invention relates to a catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons.

10 More specifically, the present invention relates to a catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally in the presence of an inert or hydrocarbon diluent.

15 Even more specifically, the present invention relates to a catalytic composition for the dehydrogenation of ethylbenzene optionally diluted in an inert product or ethane.

Processes for the dehydrogenation of alkylaromatic hydrocarbons are known. U.S. patent 6,031,143, for example, describes a process for the contemporaneous dehydrogenation of ethylbenzene and ethane in the presence of a catalytic system consisting of an inorganic carrier, such as alumina, on which various metals have been impregnated with the purpose of activating the chemical reactions involved in the process.

25 Other examples of processes for the dehydrogenation of

alkylaromatic hydrocarbons are provided in European patent 885,654 and in international patent application PCT 00/09196.

In these documents, the dehydrogenation of the alkylaromatic hydrocarbon, in particular ethylbenzene to styrene, is carried out in a unit consisting of a reactor/regenerator system both operating under fluid bed conditions. In this kind of system, the dehydrogenation unit comprises a first fluid bed dehydrogenation reactor and a second regeneration reactor of the catalyst containing coke. The latter is removed in continuous from the bottom of the first reactor and is fed to the head of the second reactor where it is maintained under fluid conditions by a mixture of fuel gas, for example methane, and preheated air. In this way, the solid slowly descends in countercurrent with the gaseous stream which rises and during this slow descent it is regenerated as the carbonaceous residues are burnt. The passage of the catalyst from one reactor to the other is guaranteed by a carrier gas such as air or nitrogen, for example.

The optimum temperature conditions in the regenerator range from 500 to 700°C and are maintained as a result of the catalytic oxidation of fuel gas (for example methane). The catalytic system therefore comprises metals active both in the dehydrogenation reaction, such as gallium or chro-

mium combined with an alkaline metal such as potassium, and in the catalytic oxidation of methane, such as platinum.

As often happens in heterogeneous catalytic systems containing multiple active components, the activity of the single components can decrease with different times. In the case of dehydrogenation, when operating with the reactor/regenerator system, the catalytic activity of the platinum is considerably lower than that of other metals such as gallium or chromium. This fact has a certain influence on the economy of dehydrogenation processes as the substitution of the platinum catalyst also implies that of the other metal catalysts, still active, as they are all impregnated on the same carrier.

The Applicant has now found that manganese, either alone or combined with platinum itself, if impregnated on an inorganic carrier such as that described in the known art, together with other dehydrogenation catalysts, is not only active in the catalytic oxidation of methane but also has a duration comparable with that of metals active in catalytic dehydrogenation.

The object of the present invention therefore relates to a catalytic composition for the dehydrogenation of alky-laromatic hydrocarbons optionally mixed with ethane, in a reactor/regenerator system, which comprises:

a) a carrier consisting of alumina in delta phase or in

theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method;

- 5 b) 0.1-35% by weight of gallium expressed as Ga₂O₃;
 c) 0.01-5% by weight of manganese expressed as Mn₂O₃;
 d) 0-100 ppm by weight of platinum;
 e) 0.05-4% by weight of an oxide of an alkaline or earth-alkaline metal;
- 10 the percentages being calculated with respect to the total of the composition.

According to a preferred embodiment of the present invention, the catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane,
15 in a reactor/regenerator system, comprises:

- 20 a) a carrier consisting of alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method;
- b) 0.2-3.8% by weight of Ga₂O₃;
 c) 0.15-1.5% by weight of manganese expressed as Mn₂O₃;
 d) 5-90 ppm by weight of platinum;
 e) 0.1-3% by weight of an oxide of an alkaline or earth-alkaline metal;
- 25

the percentages being calculated with respect to the total of the composition.

The process for preparing the catalytic system described above can be substantially carried out by means of the following steps:

- preparing one or more solutions of the components to be supported;
- dispersing the solutions on the alumina carrier modified with silica;
- 10 - drying the impregnated carrier; and
- calcining the dried carrier at a temperature ranging from 500 to 900°C;
- optionally repeating the previous steps one or twice.

In the preparation of the catalysts object of the present invention, the modified alumina carrier is in the form of particles classified as belonging to group A according to Geldart (Gas Fluidization Technology, D. Geldart, John Wiley & Sons).

The dispersion of the catalyst components on the carrier can be carried out according to the conventional techniques, such as impregnation, ion exchange, "vapour deposition" or surface adsorption. The incipient wetness impregnation technique is preferably used.

The catalyst, object of the present invention, has also proved to be surprisingly effective in the form of me-

chanical mixtures of the respective supported active metal components. A further object of the present invention therefore relates to a catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane, in a reactor/regenerator system, comprising a mechanical mixture of:

- i) 70-99.5% by weight, preferably from 80 to 95%, of a first active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, gallium, expressed as Ga₂O₃, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities, calculated with respect to the total, ranging from 0.1 to 35% by weight and 0.05 to 4% by weight, respectively;
- ii) 0.5-30% by weight, preferably from 5 to 20%, of a second active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, modified with manganese, expressed as Mn₂O₃, platinum and an oxide of an alka-

line or earth-alkaline metal supported on alumina, in quantities, calculated with respect to the total, ranging from 0.1 to 10% by weight, 0 to 1000 ppm by weight, and 0.025 to 3.95% by weight, respectively.

5 The preferred catalytic mechanical mixture is that in which the quantity of gallium ranges from 0.2 to 3.8% by weight, the quantity of manganese ranges from 0.15 to 1.5% by weight, the quantity of platinum ranges from 5 to 50 ppm by weight and the total quantity of alkaline or earth-
10 alkaline metal oxide ranges from 0.1-3% by weight.

A further object of the present invention relates to a catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane, in a reactor/regenerator system, which comprises a mechanical mixture of:
15

i) 70-99.5% by weight, preferably from 80 to 95%, of a first active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica,
20 and having a surface area lower than 150 m²/g, determined with the BET method, gallium, expressed as Ga₂O₃, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities, calculated
25 with respect to the total, ranging from 0.1 to 35% by

weight and 0.025 to 2% by weight, respectively;

ii) 0-30% by weight, preferably from 5 to 20%, of a second active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, manganese, expressed as Mn₂O₃, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities, calculated with respect to the total, ranging from 0.1 to 10% by weight and 0.025 to 3.95% by weight, respectively;

iii) 0-30% by weight, preferably from 5 to 20%, of a third active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta + theta, theta + alpha or delta + theta + alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, platinum, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities, calculated with respect to the total, ranging from 5 to 1000 ppm by weight and 0.025 to 3.95% by weight, respectively.

In this second catalytic mechanical mixture, the quantity of gallium can range from 0.2 to 3.8% by weight, the

quantity of manganese can range from 0.15-1.5% by weight, the quantity of platinum from 5 to 50 ppm by weight and the total quantity of alkaline or earth-alkaline metal oxide ranges from 0.1-3% by weight.

5 In the catalytic composition, object of the present invention, whether it consists of a single carrier on which the active metals are impregnated or various carriers impregnated separately and then mechanically mixed, the alumina carrier is modified with 0.08-5% by weight of silica
10 whereas the preferred alkaline or earth-alkaline metal is potassium or magnesium.

Also in the case of a catalytic composition consisting of a mechanical mixture of carriers impregnated separately with active metals, the alumina is used in the form of particles which are such as to be classified as belonging to group A according to Geldart (Gas Fluidization Technology, D. Geldart, John Wiley & Sons).

The catalytic system, object of the present invention, either as a single active phase or as a mechanical mixture
20 of various active phases, can be used in a process for the catalytic dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane, in a reactor/regenerator system which comprises:

A) dehydrogenating the hydrocarbon stream, optionally
25 mixed with an inert gas, in a fluid bed reactor in the

presence of a catalytic composition according to any
of the claims, at a temperature ranging from 400 to
650°C, at a total pressure ranging from 0.1 to 3 ata
and with a GHSV (Gas Hourly Space Velocity) ranging
5 from 50 to 10,000 $\text{Nl/h} \cdot \text{l}_{\text{cat.}}$; and

B) regenerating and heating the catalyst, by means of
catalytic combustion, in a fluid bed regenerator at a
temperature higher than 500°C.

The preferred alkylaromatic hydrocarbon is generally
10 ethylbenzene.

Nitrogen, methane, hydrogen, carbon dioxide and noble
gases can be used as inert gas, preferably nitrogen and
methane, with a volume ratio inert gas/hydrocarbon stream
ranging from 1 to 10, preferably from 2 to 6.

15 In the reactor/regenerator system, the catalyst in a
fluidized state circulates continuously between the two ap-
paratuses, allowing the process to be carried out in con-
tinuous.

The heat necessary for the dehydrogenation is supplied
20 by the regenerated catalyst which reaches the reactor at a
temperature higher than the reaction temperature. The cata-
lyst is maintained in a fluidized state in the reactor by
the reagent mixture, including the optional inert gas.

The reacted gas, after passing through a system of cy-
25 clones or another separation system of the powders, leaves

the reactor from above. The gas can be subsequently sent to a heat exchanger for the pre-heating of the feeding and then to the separation section where the dehydrogenation products are separated from the non-reacted charge, which
5 is recycled. The reaction by-products can be used as fuel gas in the regenerator.

In the dehydrogenation reactor, the catalyst in a fluidized state moves in countercurrent with respect to the gaseous phase. It enters the catalytic bed from above and
10 leaves the reactor from below, passing by gravity into a desorption zone so that the shifted, desorbed gas re-enters the reactor, avoiding the loss of reagents or products.

In the fluid bed reactor, the dehydrogenation reaction of step (A) is carried out at a temperature ranging from
15 450 to 650°C, at atmospheric pressure or a slightly higher value, at a GHSV ranging from 100 to 1,000 $\text{Nl/h}\cdot\text{l}_{\text{cat.}}$, preferably from 150 to 400 $\text{Nl/h}\cdot\text{l}_{\text{cat.}}$, and with residence times of the catalyst ranging from 5 to 30 minutes, preferably from 10 to 15 minutes.

20 Appropriate internal devices such as grids or cylindrical bars, capable of preventing the re-mixing of the gas and catalyst, can be horizontally arranged inside the dehydrogenation reactor, so that the stream of gas inside the reactor approaches a plug flow. The use of these internal
25 devices allows the conversion and selectivity of the hydro-

carbons to be maximized.

The catalyst is subsequently sent to the regenerator by gravity or through a pneumatic conveying system consisting of:

- 5 - a conveying line with at least one area in which the catalyst moves downwards optionally with a feeding of gas (nitrogen or methane); and
- an area in which the catalyst moves upwards, until it reaches the bed of the regenerator, by the introduc-
- 10 tion of gas.

The regeneration of the catalyst is carried out by the combustion of the carbonaceous residues with air or oxygen, whereas its heating is effected by catalytic combustion, using methane, a fuel gas or by-products of the dehydroge-

15 nation reaction, up to a temperature higher than the maximum reaction value.

The movement of the gas and solid takes place in countercurrent also in the regenerator. Air, oxygen or air diluted in nitrogen is charged into the catalytic bed whereas

20 the fuel gas is charged at different heights along the bed.

The gas leaving the regenerator, essentially consisting of nitrogen and combustion products, passes through a system of cyclones, or other system, situated in the upper part of the apparatus, to separate the entrained powders.

25 The regeneration of the catalyst in step (B) is ef-

fectected at a higher temperature with respect to the dehydrogenation temperature, at atmospheric pressure or a slightly higher value, a GHSV ranging from 100 to 1,000 $\text{Nl/h}\cdot\text{l}_{\text{cat}}$. and with a residence time of the catalyst ranging from 5 to 5 120 minutes. In particular, the regeneration temperature ranges from 500 to 700°C and the residence time ranges from 20 to 40 minutes.

The regenerated and heated catalyst is conveyed to the reactor by means of a pneumatic system analogous to that 10 described for the conveying from the reactor to the regenerator.

The dehydrogenation process, object of the present invention, is particularly suitable for the contemporaneous dehydrogenation of ethane and ethylbenzene. In this case, 15 in the dehydrogenation step (A), an ethylbenzene-ethane mixture is fed to the reactor, obtaining the contemporaneous dehydrogenation of these to give styrene and ethylene. The styrene is then separated and the ethylene, together with a stream of benzene, is fed to an alkylation unit to 20 produce ethylbenzene.

Some illustrative and non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

The catalytic combustion tests of the following examples 25 ples are carried out in a quartz fluid bed reactor with po-

rous septa also made of quartz, heated by means of external electrical resistances.

The fuel (methane) and combustion supporter (air) reach the catalytic bed from two different distributors both at the base of the catalytic bed, in order to avoid any contact before entering the catalytic bed itself. The overall composition of the feeding is 3% by volume of methane, the remainder consisting of air.

The effluent of the reactor is cooled to room temperature and the condensed water separated from the gas component which is collected in a multilayered sampling bag.

The contents of the bag are finally analyzed by means of gaschromatography to determine the CO, CO₂, CH₄, O₂, N₂ content.

The conversion of methane is finally calculated as follows:

$$\text{Conv. CH}_4 = 1 - (\% \text{CH}_4 / (\% \text{CH}_4 + \% \text{CO} + \% \text{CO}_2))$$

wherein:

%CH₄ = concentration of methane (% Vol.) in the sample collected;

%CO = concentration of carbon monoxide (% Vol.) in the sample collected;

%CO₂ = concentration of carbon dioxide (% Vol.) in the sample collected.

The catalytic dehydrogenation tests are carried out

with analogous equipment and procedures to those described in European patent 905,112.

EXAMPLE 1 (comparative) - non-promoted carrier

A microspheroidal pseudoboehmite is prepared to which
5 silica (1.2% by weight) has been added, with a particle diameter ranging from 5 to 300 μm , by the spray drying of an alumina hydrate sol and Ludox* silica.

A sample of the pseudoboehmite is calcined at 450°C for 1 hour, and then at 1140°C for 4 hours in a stream of
10 air saturated with vapor. The product obtained has a specific surface of 74 m^2/g , a porosity of 0.23 cc/g and consists of delta, theta and alpha transition aluminas.

An aliquot of this material is tested in a catalytic combustion test. The results are indicated in Table 1, from
15 which it can be deduced that the catalytic performance is unsatisfactory.

EXAMPLE 2 (reference) - Catalyst based on Gallium alone, without promoters

150 g of microspheroidal alumina prepared as described
20 in Example 1 are impregnated, by means of the "incipient wetness" procedure, with 35 ml of an aqueous solution containing 24.5 g of a solution of $\text{Ga}(\text{NO}_3)_3$ (10.71% by weight of Ga) and 14.3 g of a solution of KNO_3 (6.445% by weight of K), the remaining consisting of deionized water.

25 The impregnated product is maintained at room tempera-

* trademark

ture for 4 hours and is subsequently dried at 120°C for 24 hours. The dried product is then calcined, in a stream of dry air, at 750°C and maintained at this temperature for 4 hours.

5 The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 1.6% of SiO_2 , Al_2O_3 the complement to 100.

10 The catalytic performances in the catalytic combustion of methane, effected as described above, are indicated in table 1, from which it can be deduced that the addition of gallium to the carrier develops the performances in the catalytic combustion.

EXAMPLE 2B

15 The catalyst of Example 2, after a week of aging in dehydrogenation cycles, is tested again in the catalytic combustion of methane, under the same operating conditions described above.

 The results, indicated in Table 1, show a very limited drop in the performances.

20 EXAMPLE 3A - Catalyst based on Gallium promoted with platinum

 150 g of microspheroidal alumina prepared as described in Example 1 are impregnated, by means of the "incipient wetness" procedure, with 35 ml of an aqueous solution containing 24.5 g of a solution of $\text{Ga}(\text{NO}_3)_3$ (10.71% by weight

25

of Ga), 14.3 g of a solution of KNO_3 (6.445% by weight of K), 1.07 g of a solution of $\text{Pt}(\text{NO}_3)_2$ at 1.45% of Pt, the remaining consisting of deionized water.

5 The impregnated product is dried and calcined as in the previous example.

The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 100 ppm of Pt, 1.6% of SiO_2 , Al_2O_3 the complement to 100.

10 The catalytic performances in the catalytic combustion of methane, effected as described above, are indicated in Table 1.

A significant improvement in the catalytic performances can be observed, due to the presence of platinum.

EXAMPLE 3B

15 The same formulate as Example 3A, at the end of the catalytic combustion test, is tested in the dehydrogenation of a stream of ethylbenzene and ethane to give styrene and ethylene. Table 2 indicates the results of the catalytic performances.

20 EXAMPLE 3C

The catalyst of Example 3B, after a week of aging in dehydrogenation cycles, is tested again in the catalytic combustion of methane, under the same operating conditions described above.

25 The results, indicated in Table 1, show that the

platinum component loses its capacity of promoting combustion over a period of time.

EXAMPLE 4A (manganese)

150 g of microspheroidal alumina prepared as described
5 in Example 1 are impregnated as above with a solution consisting of 24.5 g of a solution of $\text{Ga}(\text{NO}_3)_3$ (10.71% of Ga), 14.3 g of a solution of KNO_3 (6.445% of K), 1.61 g of a solution of $\text{Mn}(\text{NO}_3)_3$ at 14.45% of Mn, the remaining consisting of deionized water.

10 The impregnated product is dried and calcined as in the previous example.

The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 0.2% of Mn (as Mn_2O_3), 1.6% of SiO_2 , Al_2O_3 the complement to 100.

15 The catalytic performances in the catalytic combustion of methane, effected as described above, are indicated in Table 1. The results indicate that manganese, like platinum, also acts as combustion promoter.

EXAMPLE 4B

20 The same formulate as Example 4, at the end of the catalytic combustion test, is tested in the dehydrogenation of a stream of ethylbenzene and ethane to give styrene and ethylene. Table 2 indicates the results of the catalytic performances.

25 EXAMPLE 4C

The catalyst of Example 4B, after a week of aging in dehydrogenation cycles, is tested again in the catalytic combustion of methane, under the same operating conditions as Example 4.

5 The results, indicated in Table 1, show that the manganese component has a better stability in its activity as combustion promoter, over a period of time.

EXAMPLE 5 (Manganese and platinum)

10 150 g of microspheroidal alumina prepared as described in Example 1 are impregnated with a solution consisting of 24.09 g of a solution of $\text{Ga}(\text{NO}_3)_3$ (10.93% of Ga), 14.4 g of a solution of KNO_3 (6.445% of K), 5.33 g of a solution of $\text{Mn}(\text{NO}_3)_3$ at 4.37% of Mn, 1.07 g of a solution of $\text{Pt}(\text{NO}_3)_2$ at 1.45% of Pt.

15 The impregnated product is dried and calcined as in the previous example.

The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 100 ppm of Pt, 0.2% of Mn (as Mn_2O_3), 1.6% of SiO_2 , Al_2O_3 the complement to 100.

20 The formulate is tested in the catalytic combustion reaction, giving the results indicated in Table 1. It can be deduced that the combination of platinum/manganese is also active in catalytic combustion.

EXAMPLE 6 (Composite mixture)

25 100 g of microspheroidal alumina, prepared as de-

scribed in Example 1, are impregnated with 24 cc of an aqueous solution containing 10.11 g of a solution of KNO_3 (6.445% of K), and 25.57 g of $\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$. The impregnated product is then treated as described in Example 2.

5 The weight composition of the catalyst is: 0.8% of K_2O , 7.8% of Mn (as Mn_2O_3), 1.5% of SiO_2 , Al_2O_3 the complement to 100.

3.5 g of this formulate are added to 122 g of the formulate of Example 2. The composite mixture has a composition similar to that of Example 4, i.e. 2.2% of Ga_2O_3 , 0.2% of Mn (as Mn_2O_3), 0.72% of K_2O , the remainder consisting of the carrier.

This mixture is tested in the catalytic combustion of methane and the results are indicated in Table 1.

15 It can be deduced that the addition of manganese, both as co-impregnated product and as a composite mixture improves the catalytic combustion.

EXAMPLE 7 (comparative) - Sample with a high platinum content

20 150 g of microspheroidal alumina prepared as described in Example 1 are impregnated as above with a solution consisting of 24.09 g of a solution of $\text{Ga}(\text{NO}_3)_3$ (10.93% of Ga), 14.3 g of a solution of KNO_3 (6.445% of K), 10.7 g of a solution of $\text{Pt}(\text{NO}_3)_2$ at 1.45% of Pt, 1.6 g of a solution of
25 $\text{Mn}(\text{NO}_3)_3$ at 14.45% of Mn.

The impregnated product is dried and calcined as in the previous example.

The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 1000 ppm of Pt, 0.2% of Mn (as Mn_2O_3),
5 1.6% of SiO_2 , Al_2O_3 the complement to 100.

The formulate tested in the dehydrogenation of a mixture of Ethylbenzene/Ethane gives the results indicated in Table 2. It can be deduced that even if the high platinum contents can on the one hand further promote the catalytic
10 combustion, on the other, they lower the performances during the dehydrogenation.

EXAMPLE 8 (test with a varying composition)

150 g of microspheroidal alumina prepared as described in Example 1 are impregnated as above with a solution consisting of 10.228 g of $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (25.8% of Ga), 2.445 g
of KNO_3 , 2.123 g of $\text{Mn}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, 0.031 g of $\text{Pt}(\text{HCO}_3)_2(\text{NH}_3)_4$, the remainder consisting of deionized water.

The impregnated product is dried and calcined as in
20 the previous example.

The weight composition of the catalyst is: 2.3% of Ga_2O_3 , 0.7% of K_2O , 70 ppm of Pt, 0.4% of Mn (as Mn_2O_3),
1.6% of SiO_2 , Al_2O_3 the complement to 100.

The formulate is tested in the catalytic combustion
25 reaction and gives the results indicated in Table 1. It can

be deduced that the increased manganese content has further improved the catalytic properties in the catalytic combustion.

EXAMPLE 8B

5 The same formulate as Example 8A is tested in the dehydrogenation of ethylbenzene in the presence of ethane. The results are indicated in Table 2.

EXAMPLE 8C

10 The same formulate as Example 8A is tested in the dehydrogenation of ethylbenzene in the presence of nitrogen. The results are indicated in Table 2.

EXAMPLE 8D

15 The same formulate as Example 8A, after a total running time of 450 hours in dehydrogenation, is tested again in the catalytic combustion of methane, under the same operating conditions as Example 8A. The results, indicated in Table 1, confirm the stability of the formulate over a period of time.

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TABLE 1

EXAMPLE	Reaction Time (°C)	GHSV (NI/lcat/h)		
		200	400	600
1	620	69-7	48.5	39.7
	640	84.5	61.8	50.9
	650	88.8	67.3	57.0
2A	620	91.9	76.0	65.6
	640	95.8	84.2	74.8
	650	97.9	87.9	79.7
2B	620	90.8	73.4	62.7
	640	95.4	83.6	74.0
	650	97.2	87.2	78.7
3A	640	98.9	91.7	81.5
	670	99.9	97.5	90.4
3C	620	91.2	71.9	59.3
	640	95.7	84.3	73.9
	650	97.2	87.3	77.9
4A	620	98.5	87.1	78.4
	640	99.3	92.5	85.5
	650	99.5	94.6	88.9
4C	620	97.4	83.1	72.9
	640	99.2	90.4	82.7
	650	99.0	93.5	86.6
	670	99.9		
5	620	98.7	90.2	81.9
	650	99.7	97.2	92.7
6	620	93.6	80.3	70.0
	640	97.9	88.0	81.3
	650	99.0	91.7	84.7
8A	600	97.6	89.1	90.8
	620	99.4	95.6	
8D	600	97.8	89.2	81.5
	620	99.7	94.8	90.1
	650		99.0	

TABLE 2

Ex.	Feeding (V%)			Press. (ata)	Reaction T (°C)	GHSV (NI/lcat/ h)	HOS	Conv. (%)		Select. (M%) STY
	EB	N ₂	C ₂ H ₆					EB	C ₂ H ₆	
3B	15	-	85	1.02	590	500	110	45.5	7.2	91.1
4B	15	-	85	1.02	590	400	119	49.1	6.9	92.6
7	20	-	80	1.02	590	400	22	39.5	4.1	93.3
7	15	-	85	1.02	590	400	45	41.1	4.3	93.5
8B	15	-	85	1.02	590	400	53	48.5	6.8	88.3
8C	15	85	-	1.02	590	400	222	53.8	--	90.6

WHAT IS CLAIMED IS:

1. A catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane comprising:
 - a) a carrier consisting of alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method;
 - b) 0.1-35%; by weight of gallium expressed as Ga₂O₃;
 - 10 c) 0.01-5% by weight of manganese expressed as Mn₂O₃;
 - d) 0-100 ppm by weight of platinum;
 - e) 0.05-4% by weight of an oxide of an alkaline or earth-alkaline metal;

the percentages being calculated with respect to the total of the composition.
2. The catalytic composition according to claim 1, comprising:
 - a) a carrier consisting of alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than 150 m²/g;
 - b) 0.2-3.8% by weight of Ga₂O₃;
 - 20 c) 0.15-1.5% by weight of manganese expressed as Mn₂O₃;
 - d) 5-90 ppm by weight of platinum;
 - e) 0.1-3% by weight of an oxide of an alkaline or earth-alkaline metal;

the percentages being calculated with respect to the total of the composition.
3. A catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane comprising a mechanical mixture of:
 - i) 70-99.5% by weight, of a first active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of

delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than $150 \text{ m}^2/\text{g}$, determined with the BET method, gallium, expressed as Ga_2O_3 , and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities ranging from 0.1 to 35% by weight and 0.05 to 4% by weight, respectively;

- ii) 0.5-30% by weight, of a second active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and
 10 having a surface area lower than $150 \text{ m}^2/\text{g}$, determined with the BET method, modified with manganese, expressed as Mn_2O_3 , platinum and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities ranging from 0.1 to 10% by weight, 0 to 1000 ppm by weight, and 0.025 to 3.95% by weight, respectively;
 the percentages being calculated with respect to the total of the composition.

4. The catalytic composition according to claim 3, comprising 80 to 95% of the first active phase.

5. The catalytic composition according to claim 3 or 4, comprising 5 to 20% of the second active phase.

- 20 6. The catalytic composition according to any one of claims 3 to 5, wherein the quantity of gallium ranges from 0.2 to 3.8% by weight, the quantity of manganese ranges from 0.15 to 1.5% by weight, the quantity of platinum ranges from 5 to 50 ppm by weight and the total quantity of alkaline or earth-alkaline metal oxide ranges from 0.1-3% by weight.

7. A catalytic composition for the dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane comprising a mechanical mixture of:

- i) 70-99.5% by weight, of a first active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, gallium, expressed as Ga₂O₃, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities ranging from 0.1 to 35% by weight and 0.025 to 2% by weight, respectively;
- 10 ii) 5-30% by weight, of a second active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, manganese, expressed as Mn₂O₃, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities ranging from 0.1 to 10% by weight and 0.025 to 3.95% by weight, respectively;
- 20 iii) 0-30% by weight, of a third active phase essentially consisting of a solid carrier based on alumina in delta phase or in theta phase or in a mixture of delta+theta, theta+alpha or delta+theta+alpha phase, modified with silica, and having a surface area lower than 150 m²/g, determined with the BET method, platinum, and an oxide of an alkaline or earth-alkaline metal supported on alumina, in quantities ranging from 5 to 1000 ppm by weight and 0.025 to 3.95% by weight, respectively;
- the percentages being calculated with respect to the total of the composition.

8. The catalytic composition according to claim 7, comprising 80 to 95% of the first active phase.

9. The catalytic composition according to claim 7 or 8, comprising 5 to 20% of the second active phase.

10. The catalytic composition according to any one of claims 7 to 9, comprising 5 to 20% of the third active phase.
11. The catalytic composition according to any one of claims 7 to 10, wherein the quantity of gallium can range from 0.2 to 3.8% by weight, the quantity of manganese can range from 0.15-1.5% by weight, the quantity of platinum from 5 to 50 ppm by weight and the total quantity of alkaline or earth-alkaline metal oxide ranges from 0.1-3% by weight.
12. The catalytic composition according to any one of claims 1 to 11, wherein the aluminum carrier is modified with 0.08-5% by weight of silica.
- 10 13. The catalytic composition according to any one of claims 1 to 12, wherein the alkaline or earth-alkaline metal is potassium or magnesium.
14. A process for the preparation of the catalytic composition as defined in claim 1 or 2, which comprises:
- preparing one or more solutions of the components to be supported;
 - dispersing the solutions on the alumina carrier modified with silica;
 - drying the impregnated carrier; and
 - calcining the dried carrier at a temperature ranging from 500 to 900°C;
 - optionally repeating the previous steps once or twice.
15. The process according to claim 14, wherein the modified alumina carrier
20 is in the form of particles classified as belonging to group A according to Geldart (Gas Fluidization Technology, D. Geldart, John Wiley & Sons).
16. A process for the preparation of the catalytic composition as defined in any one of claims 3 to 11, which comprises mixing mechanically the active phases consisting of the solid carrier based on alumina modified with silica, the alumina being in the form of particles classified as belonging to group A

according to Geldart (Gas Fluidization Technology, D. Geldart, John Wiley & Sons).

17. A process for the catalytic dehydrogenation of alkylaromatic hydrocarbons optionally mixed with ethane which comprises:

- A) dehydrogenating the hydrocarbon stream, optionally mixed with an inert gas, in a fluid bed reactor in the presence of the catalytic composition as defined in any one of claims 1 to 13, at a temperature ranging from 400 to 650°C, at a total pressure ranging from 0.1 to 3 ata and with a GHSV (Gas Hourly Space
10 Velocity) ranging from 50 to 10,000 $\text{NI/h} \cdot l_{\text{cat.}}$; and
- B) regenerating and heating the catalyst, by means of catalytic combustion, in a fluid bed regenerator at a temperature higher than 500°C.

18. The process according to claim 17, wherein the alkylaromatic hydrocarbon is ethylbenzene.

19. The process according to claim 17 or 18, wherein the inert gas is selected from nitrogen, methane, hydrogen, carbon dioxide and noble gases.

20. The process according to claim 19, wherein the inert gas is selected from nitrogen and methane.

21. The process according to any one of claims 17 to 20, wherein the volume
20 ratio inert gas/hydrocarbon stream ranges from 1 to 10.

22. The process according to claim 21, wherein the ratio ranges from 2 to 6.

23. The process according to any one of claims 17 to 22, wherein the dehydrogenation reaction of step (A) is carried out at a temperature ranging from 450 to 650°C, at atmospheric pressure or a slightly higher value, at a

GHSV ranging from 100 to 1,000 $\text{NI/h}\cdot\text{l}_{\text{cat.}}$, and with residence times of the catalyst ranging from 5 to 30 minutes.

24. The process according to claim 23, wherein the GHSV ranges from 150 to 400 $\text{NI/h}\cdot\text{l}_{\text{cat.}}$, and the residence times of the catalyst ranges from 10 to 15 minutes.

25. The process according to any one of claims 17 to 24, wherein the regeneration of the catalyst is effected with air, oxygen or air diluted in nitrogen whereas its heating is effected using methane, a fuel gas or by-products of the dehydrogenation reaction, operating at a higher temperature with respect to the
10 dehydrogenation temperature, at atmospheric pressure or a slightly higher value, a GHSV ranging from 100 to 1,000 $\text{NI/h}\cdot\text{l}_{\text{cat.}}$ and with a residence time of the catalyst ranging from 5 to 120 minutes.

26. The process according to claim 25, wherein the regeneration temperature ranges from 500 to 700°C and the residence time ranges from 20 to 40 minutes.

27. The process according to any one of claims 17 to 26, wherein in the dehydrogenation step (A) a mixture of ethylbenzene-ethane is fed to the reactor, obtaining the contemporaneous dehydrogenation thereof, using the ethane in a mixture with benzene to give the corresponding alkylaromatic.