

CONTINUOUS HYDROGENATION OF AROMATIC NITRATED COMPOUNDS USING A CATALYST HAVING A LOW ALUMINIUM CONTENT

5 The subject of the present invention is a process for the catalytic hydrogenation, carried out continuously, of aromatic nitrated compounds employing a catalyst having a low aluminium content, the conditions under which the hydrogenation is carried out being such that the residence time of the catalyst is at least 3 days.

Processes for catalytically hydrogenating aromatic nitrated compounds have
10 been known for many years. In general, these processes usually comprise two zones and peripherals. The first zone is that in which the actual hydrogenation reaction is carried out; the second zone is that in which the catalyst is separated from the reaction mixture and the peripherals denote the pipes and apparatuses (storage tanks, recycling tanks, pumps, etc.), by means of which the reaction mixture and/or the reactants are
15 conveyed, and the zone or zones for preparing the reaction mixture. It should be noted that the nitrated compounds, fresh solvent, if it is used, fresh catalyst and a catalyst suspension, coming from the reaction zone and then the separation zone, are in general mixed in this preparation zone. It is not necessary for the reaction and separation zones to be separate; this is because they may exist in the same apparatus, as for example
20 when a reactor/settling tank is used. The hydrogenation reaction is a very rapid reaction and highly exothermic; it is usually carried out in a stirred reactor or in a loop reactor. The process of separating the catalyst from the hydrogenate may be carried out in various ways, such as tangential filtration, transverse filtration and settling.

Usually, the hydrogenation processes for aromatic nitrated compounds are
25 carried out using catalysts comprising at least nickel and aluminium. Very often the catalyst used is of the Raney nickel type. This catalyst may possibly be doped with various metals, such as iron and/or chromium, for example. These catalysts are obtained by carrying out a basic treatment on an alloy comprising the catalyst metal, in this case nickel, aluminium and possibly dopant metal or metals.

30 Conventionally, the industrial processes that have been developed employ Raney catalysts whose residual aluminium content is relatively high, about 7 to 15% by weight of the catalyst.

The advantage of such catalysts is far from being questioned in the present invention. It has simply been found that these have a few drawbacks when they are
35 employed under conditions such that the reaction is carried out continuously, with long residence times of the catalyst. The same limitations apply if these catalysts are employed under high productivity conditions.

This is because, under such conditions, the parasitic oxidation of the nickel present in the catalyst becomes great. A very hard deposit is then formed over time on the walls of the reactor, of the settling tank and/or of the peripherals in the sense indicated above. This deposit, which the inventors have identified as possessing a nickel
5 alumininate structure, for example a lamellar double hydroxide of the takovite type, is due to this significant parasitic oxidation of nickel and to the concomitant presence of hydrated aluminium oxide.

This deposit creates a screen on the walls of the reactor, the settling tank and the peripherals, thereby reducing the productivity of the process whereas the intended
10 aim was in fact to increase it.

It is therefore necessary, at quite closely spaced regular intervals, to shut down the plant or the zone in question, and to clean it. However, this operation is very irksome as it requires the use of relatively powerful means to remove this deposit, such as for example the use of high-pressure lances.

15 The object of the present invention is therefore to eliminate this drawback, or at the very least to greatly reduce its undesirable consequences.

Thus, the subject of the present invention is a process for the catalytic hydrogenation of nitrated aromatic compounds, comprising a reaction zone, a separation zone and peripherals, in which process the hydrogenation is carried out
20 continuously, with a catalyst comprising at least nickel and possibly aluminium; the total aluminium content, if aluminium is present, in the catalyst being at most 5.5% by weight of the catalyst and the residence time of the catalyst in the reaction zone, separation zone and peripherals being at least three days.

The expression "total aluminium" is understood to mean the sum of aluminium
25 (0) and aluminium (+III).

It has been found that by carrying out the hydrogenation under such conditions and by employing a catalyst having, right from the start of the hydrogenation reaction, a total aluminium content much lower than that present in the catalysts developed on an industrial scale, or even containing no aluminium in certain cases, the formation of nickel
30 alumininate is greatly slowed down, or even eliminated.

A second subject of the present invention is therefore the use of a catalyst comprising at least nickel and possibly aluminium, the total aluminium content, if aluminium is present, being at most 5.5% by weight, for the purpose of limiting the formation of nickel aluminates while carrying out the catalytic hydrogenation reaction of
35 aromatic nitrated compounds continuously.

The reduction (or limitation) in the formation of nickel alumininate may especially be observed by the increase by a factor of at least 1.5, preferably at least 2, in the

operating time of the process between two shutdowns. It should be remembered that these shutdowns are necessary since the nickel aluminate deposit then prevents the plant from being operated properly (significant reduction in productivity, blockage of the pipes, especially). It has to be noted that when the amount of initial aluminum in the catalyst is low, or when there is no aluminum, it is possible to have no shutdown between two prescribed ones.

In addition, surprisingly, the use of such a catalyst does not significantly degrade the performance of the reaction, especially the yield and the consumption of catalyst. It is even remarkable to note that the use of this type of catalyst may help to increase the performance of the reaction.

As an illustration, the process employed under the conditions of the invention makes it possible to achieve a yield of hydrogenated compound (and therefore of aromatic amine) of at least 99.5% by weight.

The catalyst employed in the process is particularly suitable for achieving productivities as high as 2 mol of hydrogen converted per hour and per gram of catalyst, or indeed up to 3 mol of hydrogen converted per hour and per gram of catalyst. More particularly, the productivities achieved by the process according to the invention are between 0.1 and 3 mol of hydrogen converted per hour per gram of catalyst, preferably between 0.2 and 2 mol of hydrogen converted per hour per gram of catalyst.

Furthermore, the process according to the invention makes it possible to use, in this reaction, catalysts comprising nickel coming from other hydrogenation processes such as, for example, those employed for hydrogenating compounds comprising nitrated functional groups or nitriles, or even coming from the regeneration of catalysts employed in the same process.

Finally, it has been found that the catalysts employed the process according to the invention, even under high productivity conditions, were deactivated less rapidly than the conventional catalysts employed under the same conditions. This is because the pores of the catalysts having a lower aluminium content become blocked less rapidly.

However, other features and advantages of the present invention will become more clearly apparent on reading the description and the examples which follow.

As indicated above, the process according to the invention relates to the hydrogenation of aromatic nitrated compounds in the presence of a catalyst comprising nickel and aluminium.

According to one feature of the invention, the catalyst has a total aluminium content of at most 5.5% by weight of the catalyst. It should be noted that the catalyst has this maximum aluminium content initially, that is to say before it is engaged in the hydrogenation reaction.

According to a first particular method of implementing the invention, the total aluminium content is greater than or equal to 1% by weight with respect to the total weight of catalyst.

5 Preferably, the total aluminium content is between 1 and 5.5% by weight with respect to the total weight of catalyst. Even more advantageously, the total aluminium content in the catalyst is between 2 and 5% by weight with respect to the total weight of the catalyst.

According to a first variant of this first method of implementing the invention, the catalyst is obtained from an alloy based on nickel, aluminium and possibly at least one
10 dopant (Raney alloy).

Among the conventional dopants in this field, mention may be made of the metals of Groups IVA, VA, VIA, VIII of the Periodic Table of Elements (Supplement to the Chemical Society of France Bulletin No. 1, January 1966). Preferably, the dopant is chosen from titanium, iron and chromium, or a mixture thereof.

15 Catalysts of this type may come from various sources.

According to a first conceivable source, a catalyst is used which comes from the alkaline treatment of an alloy comprising aluminium, nickel and possibly at least one dopant, the nature of the alloy and/or the conditions under which the alloy is manufactured and/or the conditions under which the alkaline treatment is carried out
20 having the consequence that the total aluminium content does not exceed 5.5% by weight of the catalyst.

The alkaline treatment may, advantageously, be carried out as follows.

Firstly, the alkaline compound is in general a hydroxide of an alkali metal, such as lithium, sodium, potassium, caesium and rubidium.

25 This treatment may, for example, be carried out with an excess of alkaline compound with respect to aluminium. More particularly, the said alkaline compound may be employed in an amount such that the molar ratio of alkaline compound to the number of mol of aluminium present is between 1.5 and 10. Preferably, the said ratio is between 1.5 and 3.

30 Moreover, it is conventional to employ the alkaline compound in the form of an aqueous solution. More particularly, the concentration of the alkaline compound at the start of the treatment is between 10 and 50% by weight. Preferably, the said concentration is of about 15 and 30% by weight.

Advantageously, and for safety reasons, the alkaline treatment takes place under
35 conditions such that the hydrogen content in the gas phase remains below the lower explosivity limit of the air/hydrogen mixture.

Such conditions may be obtained, for example, by carrying out the said treatment under a stream of air or an inert gas such as, *inter alia*, nitrogen.

It should also be noted that the pressure at which the alkaline treatment is carried out is more particularly greater than or equal to the saturation vapour pressure of the liquid medium at the temperature of the alkaline treatment.

We remind the reader that this liquid medium comprises, *inter alia*, water, dissolved aluminium salts and the alkaline compound.

In addition, the term "saturation vapour pressure" denotes the partial pressure of the liquid medium at the temperature in question.

Furthermore, the temperature at which the alkaline treatment is carried out is preferably between 50 and 130°C. Advantageously, the said treatment is carried out at a temperature of between 60 and 90°C.

It should be pointed out that the treatment temperature may change during the alkaline treatment. More particularly, it may be advantageous to increase the temperature at the end of the treatment.

As regards the duration of the alkaline treatment, this is more particularly between 1 and 12 hours. Usually this duration is between 1 and 3 hours.

Finally, it should be noted that the aforementioned conditions are chosen in such a way that the aluminium remains in a soluble form, especially as an aluminate, during the alkaline treatment so as to be able to be separated from the remaining solid after the treatment.

A first possibility consists in using a catalyst precursor alloy having a high aluminium content. For example, alloys having an aluminium content greater than 50% by weight of the alloy may be suitable for the invention.

More particularly, the alloy has an aluminium content of less than or equal to 70% by weight of the alloy, preferably between 55 and 70% by weight of the alloy. We should point out that it would not be outside the scope of the present invention to use alloys whose aluminium content is greater than 70%. Simply, the use of this type of alloy may incur unnecessary additional costs during its treatment (cost of the raw material (alkaline compound) and effluent treatment cost).

According to one advantageous method of implementing this first possible process, and if a dopant is present in the precursor alloy, it is preferred to carry out the treatment on an alloy whose dopant content does not exceed 5% by weight of the alloy and preferably does not exceed 3% by weight of the alloy.

A second possibility consists in carrying out the alkaline treatment of the precursor alloy under conditions of a higher level than those indicated with respect to the alkaline treatment described above. Thus, among the above-mentioned conditions, all

that is required is for at least one of the conditions to be at a higher level in order for the treatment to be regarded as being carried out at a higher level. For example, these conditions may consist of a higher alkaline compound/Al molar ratio, and/or a higher initial concentration of the alkaline compound, and/or a higher temperature maintained during the treatment or temperature at the end of the treatment, and/or a longer duration.

According to one particular method of implementing this second possibility, it is also possible to carry out an additional alkaline treatment, that is to say to carry out at least one other alkaline treatment on the product resulting from a first alkaline treatment of an alloy, so as to further reduce the residual aluminium content.

Thus, it is conceivable to carry out the first alkaline treatment under conventional conditions and the second treatment under conditions at a higher level, as indicated above.

Likewise, it is possible to carry out the second treatment under conditions similar to those of the first treatment.

A third possibility consists in employing a catalyst from an alloy that has undergone a particular treatment during its manufacture. Thus, it is possible to employ catalysts obtained from an alloy that has undergone an annealing step.

More particularly according to this third possibility, the alloy ingot is subjected to a heat treatment at a temperature remaining below the peritectic temperature which results in the formation of NiAl_3 . More particularly, the temperature used in this heat treatment is between 650 and 850°C.

Advantageously, this treatment is carried out in an inert atmosphere.

This treatment rearranges the structure of the alloy and promotes the formation of phases rich in aluminium, such as NiAl_3 or the eutectic phase, for example. However, the aluminium can be easily removed from such phases during the alkaline treatment for obtaining the actual catalyst.

Of course, it would not be outside the scope of the present invention to employ a combination of the three aforementioned possibilities.

Another possible source of catalyst comes from the recycling of catalysts that have been used in hydrogenation processes, which may or may not be different from that in which the catalyst is employed.

By way of illustration, the catalysts of the Raney nickel type, doped or undoped, employed in the hydrogenation of compounds comprising nitrated functional groups or nitriles may be suitable for this variant. The consumption of the catalysts during such hydrogenation reactions results among other things in a significant drop in the residual aluminium content.

Before it is used in the process according to the invention, the catalyst is advantageously subjected to a first washing operation using water so as to remove any trace of organic compounds present during the previous process. The resulting catalyst then undergoes a regeneration step consisting in carrying out at least an alkaline washing operation. The purpose of this operation is to remove all or some of the oxidized aluminium present in the catalyst.

The conditions detailed above for the alkaline treatments may be used in this type of washing.

However, according to one advantageous method of implementing this variant, the said alkaline washing is carried out at a temperature of less than or equal to 150°C, although higher temperatures may be envisaged depending on the type of apparatus employed and the energy sources available. More particularly, the temperature is greater than or equal to 50°C, preferably between 80 and 140°C.

The alkaline washing may be carried out at atmospheric or higher pressure, depending on the characteristics of the apparatuses employed. It should be noted that there is no significant advantage in carrying out the treatment at total pressures greater than 30×10^5 Pa.

With regard to the alkaline compound, this may be employed at a concentration of less than or equal to 35% by weight in water.

This regeneration step may also be carried out advantageously with a hydrogen pressure so as to possibly further reduce some of the oxidized nickel.

In such a case, the treatment is carried out more particularly with a hydrogen partial pressure of at least 10^5 Pa (1 bar). The hydrogen partial pressure may be as high as possible, depending on the equipment used. However, this hydrogen partial pressure is advantageously less than or equal to 30×10^5 Pa (30 bar). The total pressure in the case of a treatment in hydrogen is advantageously between 6 and 30×10^5 Pa (6 – 30 bar).

A second variant of the first method of implementing the invention consists of the use of catalysts comprising nickel and aluminium and a support.

The nickel may possibly be combined with at least one dopant metal such as those belonging to Groups IVA, VA, VIA, VIII of the Periodic Table of Elements, preferably from titanium, iron and chromium, or a mixture thereof.

The said support is more particularly chosen so that it is stable under the reaction conditions.

More particularly, the support comprises aluminium (more particularly in the form of alumina) combined with at least one oxide chosen from zirconium, titanium and silicon oxides, by themselves or as mixtures.

It should be noted that the catalyst is such that the total aluminium content of the catalyst, whatever its degree of oxidation, fulfils the conditions indicated above, namely that it does not exceed 5.5% of the total weight of the catalyst.

The amount of support is more particularly between 25 and 80% by weight of catalyst, preferably between 30 and 65% by weight of catalyst.

This type of catalyst is usually obtained by precipitating, on the support, a nickel salt and possibly at least one salt of a dopant metal. The catalyst is then separated, for example by filtration, then dried and calcined at a high enough temperature to convert the nickel hydroxide, and possibly the salt or hydroxide of the dopant metal, into oxides. Once this step has been carried out, the catalyst undergoes a treatment during which some of the nickel is reduced. This reduction is generally carried out at high temperature in a reducing atmosphere, such as hydrogen.

It would be possible to employ, in the reaction according to the invention, a supported catalyst, like that just described, which had been used beforehand in another hydrogenation process. In such a case, it is preferable, before the said spent catalyst is used at all in the process according to the invention, to carry out a water washing step, or even an alkaline washing step, so as to remove any trace of organic compounds deriving from the previous process. After this washing step, it may be recommended to carry out a reduction treatment, preferably at high temperature in a reducing atmosphere such as hydrogen.

According to a second particular method of implementing the invention, the catalyst comprises nickel but not aluminium.

According to this method of implementation, the catalyst employed comprises a support which contains no aluminium. The statements made above with regard to supported catalysts comprising aluminium (preparation; origin (fresh or recycled), treatment of the recycled catalyst before it is introduced into the hydrogenation process according to the invention) remain valid for this method of implementation, given that aluminium is not present in this particular method of implementation.

The catalyst that has just been mentioned is therefore employed in a reaction involving the catalytic hydrogenation of nitrated aromatic compounds, carried out continuously.

According to an important feature of the process according to the invention, the residence time of the catalyst is at least 3 days.

Within the meaning of the present invention, the residence time (T_{res}) is defined as follows:

$$T_{res} = \frac{\text{Catalyst employed}}{\text{Catalyst consumed} \times \text{Aminated compound production}}$$

Catalyst employed: Amount of catalyst in the reaction zone, separation zone and peripherals, expressed in kg;

Catalyst consumed: Amount of catalyst consumed in the process (amount of catalyst which is purged and not subsequently reinjected into the process); expressed in kg of purged catalyst per metric ton of aminated compound produced;

Aminated compound production: Amount of aminated compound produced, expressed in metric tons per day.

Very often, the residence time of the catalyst in these zones is of the order of several weeks.

5 The term "nitrated aromatic compounds" is understood to mean, in particular, compounds comprising at least one nitrated functional group, and preferably at least two nitrated functional groups, and at least one C₆-C₁₄, preferably C₆-C₁₀ aromatic unit which may or may not be substituted with one or more C₁-C₁₀ linear, cyclic or branched, saturated or unsaturated, hydrocarbon radicals and/or one or more hydroxyl radicals.

10 More specifically, the aforementioned hydrocarbon radicals, possibly substituting the said aromatic units, may be chosen from C₁-C₁₀, preferably C₁-C₆, alkyl, aryl, alkylaryl and arylalkyl radicals.

As aromatic units, mention may especially be made of benzene rings and naphthalene rings, which may or may not be substituted with one or more methyl, ethyl, 15 propyl, butyl, pentyl or hexyl radicals and/or isomers thereof.

The process according to the invention may be implemented using at least one compound chosen from mononitrobenzene, dinitrobenzene, mononitrotoluene, dinitrotoluene, paranitrocumene and orthonitrophenol.

20 The process according to the invention is employed highly advantageously with a mixture of dinitrotoluene isomers.

The aromatic nitrated compounds may be employed in the presence of a solvent for the said compounds.

According to a first variant, the solvent employed is chosen from aliphatic alcohols or cyclic ethers, by themselves or as a mixture.

More particularly, methanol, ethanol, propanol or isopropanol, by themselves or as a mixture, is used as aliphatic alcohol.

As cyclic ethers, mention may be made of dioxane and tetrahydrofuran, by themselves or as a mixture.

5 According to this variant, before the aromatic nitrated compounds are introduced into the reaction zone they are dissolved in the aforementioned solvent or solvent mixture.

The concentration of nitrated compounds in the solvent or solvent mixture may vary over a wide range. However, single-phase mixtures, that is to say mixtures for 10 which the solubility limit of the nitrated compound or compounds is not reached for the solvent or mixture in question, are used. Without intending to be limited thereby, the concentration range is less than or equal to 25% by weight.

According to a second preferred variant of the invention, the solvent employed is the hydrogenated compound. If this variant is adopted, the aromatic nitrated compounds 15 are introduced in the liquid or molten state.

This variant is advantageous in that it does not dilute the reactant, as is the case when a solvent or solvent mixture is used. This helps in particular to maintain a high process productivity. Moreover, this variant obviates any additional step of separating the products from the solvent(s) used during the reaction, which step runs the risk of 20 loss of hydrogenated products.

The instantaneous content of nitrated compounds in the reaction zone is maintained as low as possible. Usually, measures are taken to ensure that it does not exceed 1000 ppm. This content of nitrated compounds in the reactor is maintained by adjusting the feed rate of nitrated compounds so that they are almost instantly reduced 25 by the catalyst as soon as they are introduced into the reactor. The process according to the invention is very suitable for operating at very high productivity levels, that is to say the aromatic nitrated compound is fed almost at the maximum rate at which it can be absorbed by the reactor/catalyst pair.

The hydrogen employed is more particularly pure hydrogen. The expression 30 "pure hydrogen" is understood to mean a gas containing at least 99% hydrogen and more particularly at least 99.9% hydrogen. It should be noted that it would not be outside the scope of the present invention to carry out the hydrogenation reaction with diluted hydrogen, although this provides no particular advantage to the reaction.

Preferably, the hydrogen is fed in the stoichiometric amount. However, it would 35 not be outside the scope of the present invention to carry out the hydrogenation with hydrogen in excess compared with stoichiometry. Such conditions may be

advantageous for meeting hydrodynamic criteria, more particularly for optimizing gas/liquid transfer of some technologies.

The hydrogen pressure in the reactor advantageously varies between 5 and $70 \cdot 10^5$ Pa (5 and 70 bar), preferably between 10 and $50 \cdot 10^5$ Pa (10 and 50 bar).

5 This gas is fed by any means known to those skilled in the art for enabling this gas to be distributed homogeneously within the reactor.

Preferably, the reaction is carried out in a stirred reactor or in a loop reactor.

The temperature is more particularly between 50 and 200°C.

10 After the hydrogenation reaction, the reaction mixture is separated from the catalyst by settling or filtration, using conventional methods.

Of course, the amount of reaction mixture separated corresponds to the amount of nitrated compound, possibly in the presence of the solvent, introduced into the reaction zone, so as to maintain stable operating conditions.

15 The reaction mixture separated from the catalyst is then treated according to its composition and its subsequent use.

Thus, if the reaction is carried out with a solvent, the hydrogenated product obtained is separated, for example, by distillation. It should be noted that, depending on the choice of solvent and the subsequent step to which the hydrogenated products will be subjected, this separation step may be unnecessary.

20 Next, the aromatic hydrogenated product can be employed in a phosgenation reaction, after being dehydrated, so as to obtain aromatic isocyanates, which are intermediates in the production of polyurethanes, or else, if necessary, distilled in order to separate the various isomers obtained.

Specific tests, which do not limit the invention however, will now be presented.

25

EXAMPLE 1

A standard undoped Raney nickel containing 8% total aluminium by weight was evaluated using two tests (Test 1 and Test 2).

30

a) Test 1:

50 g/h of a mixture of dinitrotoluene (DNT) isomers were fed continuously into a reactor containing 0.7 g of Raney nickel at 150°C under a hydrogen pressure of 20 bar.

35 The DNT feed was continued until the DNT content in the reactor exceeded 1000 ppm.

The hydrogen feed was guided by the progress of the reaction in order to remain at constant pressure in the reactor.

The reaction was stopped after 6 hours.

The yield of the reaction at $t = 4$ hours was about 99%.

b) Test 2:

5 A sample of the initial catalyst (not having undergone the hydrogenation) was introduced with a mixture of toluenediamine (TDA) isomers and water into a glass tube called a Carius tube, which was sealed and then left for 1 month at 150°C under autogenous pressure.

10 After one month, the tube was opened; the catalyst was irrecoverable and extremely hard.

The structure of the catalyst was found by X-ray diffraction to be that of a nickel aluminate (takovite). This structure is the same as that of the deposit (screen) observed on the walls of apparatuses used on an industrial scale.

15 **EXAMPLE 2**

The catalyst employed was a Raney nickel recovered from a nitrile hydrogenation unit containing 3.5% total aluminium by weight. The catalyst was firstly washed with water and then dilute (1N) sodium hydroxide and then again with water.

20 The catalyst was then evaluated within the same tests as those described in Example 1.

a) Test 1:

Test 1 of Example 1 was repeated.

The results were as follows:

- 25 - the reaction was stopped after 8 hours;
- the reaction yield at $t = 4$ h was 99.2%.

b) Test 2:

Test 2 of Example 1 was repeated.

30 The results were as follows:

- the tube was opened after 1 month; the catalyst was recoverable and slightly hard.

Using X-ray diffraction, the structure of the catalyst was basically that of nickel. It contained a small proportion of nickel aluminate (at least half the amount of that in the catalyst of Example 1).

35

EXAMPLE 3

The catalyst employed in this example was an undoped nickel-based supported catalyst containing about 2 % total aluminium by weight, in the form of alumina, 2 to 6%
5 ZrO_2 , silica and nickel with a total nickel content of 55% by weight.

The catalyst was evaluated using the same tests as those described in Example
1.

a) Test 1:

10 Test 1 of Example 1 was repeated.

The results were as follows:

- the reaction was stopped after 9 hours;
- the reaction yield at $t = 4$ h was close to 99.2%.

15 **b) Test 2:**

Test 2 of Example 1 was repeated.

The results were as follows:

- when the tube was opened, after 1 month, the catalyst was recoverable and not
hard.

20 Using X-ray diffraction, the structure of the catalyst was found to be basically the same as that observed in the fresh catalyst.

CLAIMS

1. Process for the catalytic hydrogenation of nitrated aromatic compounds, comprising a reaction zone, a separation zone and peripherals, characterized in that the hydrogenation is carried out continuously, with a catalyst comprising at least nickel and possibly aluminium, in that the total aluminium content, if aluminium is present, in the catalyst is at most 5.5% by weight of the catalyst and in that the residence time of the catalyst in the reaction zone, separation zone and peripherals is at least three days.
2. Process according to the preceding claim, characterized in that the total aluminium content is greater than or equal to 1% with respect to the weight of catalyst, and preferably between 2 and 5% by weight with respect to the same reference.
3. Process according to either of the preceding claims, characterized in that the catalyst is obtained from an alloy comprising nickel, aluminium and possibly at least one dopant.
4. Process according to the preceding claim, characterized in that the dopant(s) is/are chosen from the metals of Groups IVA, VA, VIA, VIII of the Periodic Table of Elements, preferably from titanium, iron and chromium, or a mixture thereof.
5. Process according to either of claims 1 and 2, characterized in that the catalyst comprises a support.
6. Process according to the preceding claim, characterized in that the support comprises aluminium oxide combined with at least one oxide chosen from zirconium, titanium and silicon oxides, by themselves or as mixtures.
7. Process according to claim 1, characterized in that the catalyst comprises a support containing no aluminium.
8. Process according to any one of the preceding claims, characterized in that the hydrogenation is carried out at a temperature of between 50 and 200°C.
9. Process according to any one of the preceding claims, characterized in that the hydrogenation is carried out at a pressure of between 5 and 70.10⁵ Pa.



10. Process according to any one of the preceding claims, characterized in that the conditions under which the reaction is carried out are such that the productivity is at most 3 mol of converted hydrogen per hour and per gram of catalyst, preferably at most 2 mol of converted hydrogen per hour and per gram of catalyst.

11. Process according to any one of the preceding claims, characterized in that the aromatic nitrated compound is chosen from compounds comprising at least one nitrated functional group, and preferably at least two nitrated functional groups, and at least one C₆-C₁₄, preferably C₆-C₁₀ aromatic unit which may or may not be substituted with one or more C₁-C₁₀ linear, cyclic or branched, saturated or unsaturated, hydrocarbon radicals and/or one or more hydroxyl radicals.

12. Process according to any one of the preceding claims, characterized in that the hydrogenation is carried out in the presence of a solvent for the aromatic nitrated compounds.

13. Process according to claim 12, characterized in that the solvent is chosen from aliphatic alcohols or cyclic ethers, by themselves or as a mixture.

14. Process according to claim 12, characterized in that the reaction is carried out in the presence of a solvent which is the hydrogenated compound.

15. Use in a process for the continuous catalytic hydrogenation of nitrated aromatic compounds, comprising a reaction zone, a separation zone and peripherals, employing a catalyst comprising at least nickel and possibly aluminium, the total aluminium content, if aluminium is present, being at most 5.5% by weight of the catalyst, for the purpose of limiting the formation of nickel aluminates.

