PATENT SPECIFICATION (11) 1 562 780

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(21) Application No. 53715/77 (22) Filed 23 Dec. 1977
(31) Convention Application No. 7 639 218 (32) Filed 24 Dec. 1976 in
(33) France (FR)
(44) Complete Specification published 19 March 1980
(51) INT. CL.[3] B01J 23/70
C07B 1/00
(52) Index at acceptance
B1E 1167 1257 1258 1260 1296 1322 1372 1461 1462 1463 1731 DD

(72) Inventors GERARD HILLION
CHRISTIAN LASSAU

(19)

(54) CATALYSTS AND PROCESSES FOR HYDROGENATION OF UNSATURATED COMPOUNDS

(71) We, INSTITUT FRANCAIS DU PETROLE, a body corporate organised and existing under the laws of France, of 4 avenue de Bois-Preau, 92502 Rueil-Malmaison, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns the hydrogenation of unsaturated compounds in liquid phase using a soluble catalyst obtained by reacting an organometallic reducing compound with at least one transition metal carboxylate and at least one strong carboxylic acid.

It is already known that hydrogenation catalysts can be prepared by contacting a transition metal compound with a reducing compound, for example an alkoxyaluminium hydride or a trialkyl-aluminium. See for example USP 3,663,635 or 3,784,481. The Chemical and Engineering News publication of March 4, 1963, pages 34-35, discloses the preparation of catalysts by reacting triisobutyl aluminium with chromium stearate or manganese acetate. According to the author, the solubility of these catalytic systems is doubtful in opposition to that of the catalytic systems prepared from an acetylacetonate, for example, chromium acetylacetonate or manganese acetylacetonate. Notwithstanding this advantage of solubility, the acetylacetonates are not widely used, in view of their high cost.

The activity of the catalysts of doubtful solubility, obtained from carboxylates, is not entirely satisfactory, particularly as concerns the reaction velocity.

This invention is based on the discovery that an excellent catalyst for hydrogenating unsaturated compounds, preferably in homogeneous or substantially homogeneous phase, can be obtained by reducing with an organometallic compound or a metal hydride, (a) a carboxylate of a transition metal derived from an organic carboxylic acid whose pK_a in water at 25°C is lower than 7 and (b) at least one organic carboxylic acid whose pK_a in water at 25°C is lower than 7, the molar ratio of the carboxylic acid to the transition metal carboxylate being from 0.05 : 1 to 1 : 1. With such a catalyst, the reaction velocity is generally increased.

The carboxylic acid has a pK_a in water at 25°C lower than 7. In case of a too low solubility in water, the pK_a is determined by using correlations between the pK_a of the other carboxylic acids determined in water and in an alcohol such as methanol or ethanol. As a rule, these are acids with 1 to 25 carbon atoms, preferably 6 to 25 carbon atoms, per molecule and that contain only hydrogen, carbon and oxygen.

Examples of organic carboxylic acids which can be used according to the invention are hexanoic, heptanoic, iso-heptanoic, octanoic, decanoic, palmitic, stearic, naphthenic, toluic and oleic acids.

A preferred general formula of these acids is R-COOH, where R is a univalent hydrocarbon radical of 5 to 24 or more carbon atoms. R may be substituted with groups which are not detrimental to the reaction, for example -OH, -CO- or additional -COOH groups.

The preferred transition metals are cobalt and, above all, nickel. These metals may be associated with other metals having a co-catalytic effect, as described for example in the Belgian Patent 813,996 or French Patent 2,249,709.

The metal carboxylate, particularly cobalt or nickel carboxylate, is a salt of the metals with one of the above carboxylic acids of pK_a lower than 7. Examples of such carboxylates are cobalt diacetate, nickel diacetate, a nickel naphthenate, nickel stearate, cobalt ethylhexanoate, nickel ben-

zoate, nickel decanoate and nickel oleate. Examples of additional salts are iron, zinc, molybdenum or zirconium stearate or heptanoate. The carboxylates from acids with 6 to 25 carbon atoms are preferred.

These compounds are usually used as solutions in solvents which may be, for example, a saturated, unsaturated or aromatic hydrocarbon, a mixture of these hydrocarbons or an ether.

The reducing compounds comprise organometallic compounds or metal hydrides whose metal is lithium, sodium or aluminium or mixed derivatives (organometal compounds or hydrides) of aluminium and sodium or lithium. These compounds have usually at least one carbon-metal or hydrogen-metal bond, the metal being preferably aluminium, lithium or sodium. A compound of the formula Al R_1 R_2 R_3 may, for example, be used, where R_1 is hydrogen or a univalent hydrocarbon radical and each of R_2 and R_3 is a hydrogen or halogen atom or a univalent hydrocarbon, (univalent hydrocarbon)-oxy, amino, alkylamino or dialkylamino radical.

A preferred class of reducing compounds complies with the above formula where at least one of R_1, R_2 and R_3 is hydrogen, the others being univalent hydrocarbon-oxy radicals.

Non-limitative examples are diethoxyaluminium hydride, isobutoxyaluminium dihydride, diethoxyaluminium sodium dihydride, butyl lithium, ethyl sodium, naphthalene sodium, triethylaluminium, chlorodiethylaluminium, triisobutylaluminium, diethyl tert-butoxyaluminium, diethoxyethylaluminium, diisobutylaluminium hydride, lithium aluminium hydride, sodium aluminium hydride and their derivatives having a hydrocarbon or alkoxy substituent.

The reducing compound may be used in the pure state or in a solvent, for example a hydrocarbon or an ether.

The method of manufacture of the catalyst is not critical. For example, a solution of the metal carboxylate and acid may be poured into a solution of the reducing compound, or a solution of the reducing compound may be poured into the solution of the metal carboxylate and acid, or a solution of the reducing compound is poured into a solution of the metal carboxylate and a solution of the carboxylic acid is then added, or vice versa. The reducing compound may be introduced into a common solution of the carboxylic acid and the carboxylates, or the carboxylic acid is added to the reaction product of the carboxylates with the reducing agent. The catalyst is preferably prepared in an inert solvent, in the absence of the compound to be hydrogenated. An active catalyst may be sometimes prepared in the presence of the compound to be hydrogenated or the reaction product. The inert solvent is preferably an aliphatic or cycloaliphatic saturated hydrocarbon or an aromatic hydrocarbon (the latter preferably at moderate temperature).

The ratio of the number of molecules of the reducing compound to the number of atoms of the transition metal is generally between 0.5 : 1 and 10 : 1, preferably between 1.5 : 1 and 6 : 1.

The manufacture of the catalyst may be effected, for example, at 0 - 200°C, preferably 70 - 160°C. This manufacture may be carried out in an inert atmosphere, for example under nitrogen or hydrocarbon gas or in a reducing atmosphere, for example under hydrogen pressure. The latter method is preferred, provided the hydrogen partial pressure is at least 0.1 kg/cm^2. The so-prepared catalysts retain their activity over a long period, possibly one year or more. This beneficial effect appears to be attributable to hydrogen stabilisation of the catalyst during manufacture thereof.

When using the so-obtained catalyst, the hydrogen pressure may range from 0.1 to 100 bars, preferably from 2 to 50 bars.

The reaction temperature may range from 0 to 300°C, preferably 10 to 250°C.

The concentration of the catalyst is usually low, from 5 to 1,500 ppm, preferably 20 to 1,000 ppm by weight of metal with respect to the total feedstock.

The ratio by volume of the injected catalytic solution to the volume of the compound to be hydrogenated is usually between 0.001% and 10%.

Depending on the operating conditions, the hydrogenation may be partial or total; in particular, a selective partial hydrogenation may be obtained when conducting a hydrogenation reaction in several successive steps.

The unsaturated hydrogenable compounds are particularly hydrocarbons with 2 - 40, for example 2 - 20, carbon atoms, irrespective of the number and the type of unsaturation, such as acetylenic, ethylenic, polyolefinic and aromatic hydrocarbons, and unsaturated compounds having one or more oxygen or nitrogen atoms, in addition to the carbon and hydrogen atoms, such as saturated and unsaturated ketones, unsaturated esters, saturated and unsaturated aldehydes, unsaturated alcohols and ethers, saturated and unsaturated nitriles, unsaturated sulfones, unsaturated amines, imines, saturated and unsaturated nitro derivatives, or phenols. Unsaturated polymers may also be hydrogenated, for example polybutadiene or polyisoprene.

Examples of hydrogenable compounds are butadiene, cyclododecatriene, vinyl-

acetylene, cyclopentadiene, butenes, cyclopentene, benzene, alkylbenzenes, phenol and its derivatives, alkyldiphenyls, alkylnaphthalenes, for example toluene, xylenes, methylnaphthalene, propionitrile, adiponitrile, oleonitrile, 1,4-dicyanobutene, benzonitrile, vinylethylsulfone, vinylethylketone, unsaturated fatty oils and ethyl linoleate.

When operating continuously, it is more advantageous to inject the previously prepared catalytic solution into the duct for feeding the compound to be hydrogenated, for example propylene, butadiene, benzene or naphthalene, rather than directly into the reaction vessel.

When operating in continuous manner, the hydrogenation product may be discharged by vaporisation. The latter technique is particularly advantageous when the reaction product is, for example, propane, butenes, butane or cyclohexane. This product may be vaporized and then condensed. A fraction of the exhausted catalyst may be discharged continuously or periodically, as desired. It is however sometimes advantageous to let the catalyst accumulate in the reaction vessel.

According to another preferred operating manner, a reactor containing fixed catalyst is arranged after one or more reactors operated in homogeneous phase as above described; the reaction thus terminates in heterogeneous phase, either in gas phase or in liquid phase.

The catalyst may be used in a batch process or in a continuous process.

The following examples illustrate the invention in a non-limitative manner. In these examples, the reaction velocity is the average velocity for a 90% conversion of the starting material. Examples 1 to 4, 6 and 11 to 13 do not illustrate the invention.

Sodium stearate is prepared by reacting sodium hydroxide with stearic acid. After washing, sodium stearate is dissolved into water and nickel chloride hydrate is then added; a green precipitate of nickel stearate is then collected; results of the elementary analysis conform to the theoretical values. This general method of preparation of the salts of transition metals has also been used in the following examples, with other carboxylic acids, to prepare nickel or cobalt salts.

— *EXAMPLE 1*

0.6 millimole of cobalt stearate is dissolved in 10 milliliters of benzene. A solution of $NaAlH_2$ (O-tert-butyl)$_2$ in tetrahydrofuran is then added at 25°C in nitrogen atmosphere, in an aluminum : cobalt molar ratio of 2 : 1. The so-prepared catalyst is used to hydrogenate cyclohexene at 50°C under 30 bars hydrogen pressure. Cyclohexane forms at a rate of 2.5 mole.liter^{-1}.mn^{-1}. Cyclohexane is obtained in quantitative yield.

— *EXAMPLE 2*

Example 1 is repeated with the cobalt salt of dodecanoic acid. The result is the same.

— *EXAMPLE 3*

Example 1 is repeated by using the cobalt salt of octoic acid. The same result is obtained.

These examples show that the nature of the carboxylic acid has no influence on the reaction velocity.

— *EXAMPLE 4*

Example 2 is repeated with the cobalt salt of decanoic acid, except that the reducing agent is $NaAlH_2$ (OCH_2 CH_2 OCH_3)$_2$ in benzene solution in aluminum : cobalt molar ratio of 2 : 1. The hydrogenation rate is 2.0 mole.liter^{-1}.mn^{-1} and cyclohexane is obtained quantitatively.

— *EXAMPLE 5*

Example 4 is repeated by adding decanoic acid to the solution of the cobalt salt in a molar ratio of the acid to the salt of 0.2 : 1. The velocity is 3.0 mole-liter^{-1}.mn^{-1} and cyclohexane is obtained quantitatively.

— *EXAMPLE 6*

Example 2 is repeated, with the use of the nickel salt of decanoic acid instead of the cobalt salt, in the same molar proportion. The velocity is 2.2 mole-liter^{-1}.mn^{-1}, and the yield of cyclohexane is quantitative.

— *EXAMPLE 7*

Example 6 is repeated, except that decanoic acid is added to the nickel solution in an acid to metal molar ratio of 0.2 : 1, prior to the addition of the reducing agent. The velocity is 3.0 mole-liter^{-1}.mn^{-1}, and the yield of cyclohexane is quantitative.

— *EXAMPLE 8*

Example 7 is repeated, except that the catalyst is used one year after its manufacture. The velocity is 1.5 mole-liter^{-1}.mn^{-1}; the cyclohexane yield is quantitative.

— *EXAMPLE 9*

Example 7 is repeated, except that the catalyst is prepared in a hydrogen stream, the hydrogen partial pressure being 0.2 to 0.3 bars. The same result is obtained.

— *EXAMPLE 10*

Example 9 is repeated, except that the catalyst is used one year after its manufacture. The same result is obtained, which shows the good stability of this particular type of catalyst.

— *EXAMPLE 11*

0.6 millimole of nickel stearate is dissolved in 10 milliliters of benzene. A solution of triethylaluminum in benzene is added in a nickel : aluminum molar ratio of 3 : 1. The resulting solution is used as catalyst to hydrogenate benzene at 180°C under 7 atm. hydrogen pressure. The catalyst concentration, expressed as nickel, is 35 millimoles per liter. The reaction is ter-

minated in 2 hours. Cyclohexane is obtained quantitatively.

— *EXAMPLE 12*

Example 11 is repeated, except that nickel stearate is replaced by the nickel salt of decanoic acid in the same molar proportion. The result is unchanged.

— *EXAMPLE 13*

A catalyst is made from 1.4 millimole nickel octoate, 0.35 millimole iron octoate and 5.6 millimole triethylaluminum; it is used to hydrogenate 100 g of bis-phenol A dissolved in 100 g of 2-ethyl hexanol at 170°C under 23 bars hydrogen pressure. After 5 hours of reaction, hydrogen is no longer absorbed, the theoretical hydrogen amount being already absorbed. Dicyclohexanol propane is obtained quantitatively.

— *EXAMPLE 14*

Example 12 is repeated, except that decanoic acid is added to the solution of the nickel salt in a molar ratio of the acid to nickel of 0.2 : 1. The reaction is terminated within 45 minutes. The cyclohexane yield is quantitative.

— *EXAMPLE 15*

Example 13 is repeated, except that octoic acid is added to the nickel and iron solution in a molar ratio of the acid to the metal (nickel + iron) of 0.20 : 1. The absorption of hydrogen ceases after 4 hours of reaction and dicyclohexanol propane is obtained quantitatively.

— *EXAMPLE 16*

Example 14 is repeated, except that the solvent of the nickel salt is a 50 : 50 by volume mixture of di-isopropyl ether and benzene. The reaction is terminated within 35 minutes. The cyclohexane yield is quantitative.

— *EXAMPLE 17*

Example 14 is repeated, except that the solutions of the metal salt and of the reducing agent are admixed under a hydrogen pressure of 0.2 to 0.3 bar. The reuslt is unchanged.

— *EXAMPLE 18*

Example 14 is repeated, except that the catalyst has been stored for 1 year before use. The reaction is terminated within 60 minutes. The cyclohexane yield is quantitative.

— *EXAMPLE 19*

Example 17 is repeated, except that the catalyst was prepared one year earlier. The result remains unchanged.

WHAT WE CLAIM IS:

1. A process for hydrogenating an unsaturated compound in liquid phase by means of hydrogen and a soluble catalyst, in which the soluble catalyst is a product obtained by reacting at least one reducing agent selected from organometallic compounds and metal hydrides with (a) at least one carboxylate of a transition metal derived from an organic carboxylic acid whose pK_a in water at 25°C is lower than 7, and (b) at least one organic carboxylic acid whose pK_a in water at 25°C is lower than 7, the molar ratio of the carboxylic acid to the transition metal carboxylate being from 0.05 : 1 to 1 : 1 and the catalyst concentration being 5 to 1500 ppm by weight of metal with respect to the total feedstock.

2. A process according to Claim 1 in which the catalyst is prepared in an inert solvent in the absence of the compound to be hydrogenated.

3. A process according to Claim 2 in which the inert solvent is a saturated aliphatic or cycloaliphatic hydrocarbon or an aromatic hydrocarbon.

4. A process according to any preceding claim in which the carboxylate (a) is a nickel and/or cobalt carboxylate.

5. A process according to any preceding claim in which the organic carboxylic acid contains 6 to 25 carbons atoms in the molecule.

6. A process according to any preceding claim in which the carboxylate (a) is a derivative of a $C_{6\text{-}25}$ carboxylic acid.

7. A process according to any preceding claim in which the reducing agent has the formula Al R_1 R_2 R_3 in which R_1 is a hydrogen atom or a univalent hydrocarbon radical and each of R_2 and R_3 is a hydrogen or halogen atom or a univalent hydrocarbon, (univalent hydrocarbon)-oxy, amino, alkylamino or dialkylamino radical.

8. A process according to any preceding claim in which the reducing agent is a (univalent hydrocarbon)-oxyaluminium hydride.

9. A process according to one of Claims 1 to 8, in which the catalyst has been prepared under a hydrogen partial pressure of at least 0.1 kg/cm^2.

10. A process according to Claim 1, substantially as hereinbefore described with reference to any one of Examples 5, 7 to 10 and 14 to 19.

11. A catalyst for use in the process of any one of Claims 1 to 10, that is the product obtained by reducing, with an organometallic compound or a metal hydride, (a) a carboxylate of a transition metal derived from an organic carboxylic acid whose pK_a in water at 25°C is lower than 7, and (b) at least one organic carboxylic acid whose pK_a in water at 25°C is lower than 7, the molar ratio of the carboxylic acid to the transition metal carboxylate being from 0.05 : 1 to 1 : 1.

12. A catalyst according to Claim 11 in which the organic acid has 6 to 25 carbon atoms to the molecule and the transition metal of the carboxylate is nickel or cobalt.

13. A catalyst according to Claim 11,

substantially as hereinbefore described with reference to any one of Examples 5, 7 to 10 and 14 to 19.

14. A hydrogenated product produced by a process according to any one of Claims 1 to 10.

15. A hydrogenated product produced by the use of a catalyst according to any one of Claims 11 to 13.

For the Applicants
D. YOUNG & CO.
Chartered Patent Agents
9 & 10 Staple Inn
LONDON WC1V 7RD

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1980.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.