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(54) **HYDROGENATION OF AROMATIC NITROCOMPOUNDS TO AROMATIC AMINES**
HYDRIERUNG AROMATISCHER NITROVERBINDUNGEN ZU AROMATISCHEN AMINEN
HYDROGENATION DE COMPOSES NITRO-AROMATIQUES EN AMINES AROMATIQUES

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(56) References cited:
EP-A- 0 629 442
WO-A-89/08659
WO-A-96/01304
WO-A-97/38955
US-A- 2 891 094

- **ACS SYMPOSIUM SERIES, (1996), 626 (Green Chemistry), 208. National Meeting of the American Chemical Society, August 21-25, 1994, PAUL T. ANASTAS, Editor et al., DAVID A. MORGENSTERN et al., "Supercritical Carbon Dioxide as a Substitute Solvent for Chemical Synthesis and Catalysis", pages 132-151.**

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Description

[0001] The present invention concerns a method in accordance with the preamble of claim 1. for hydrogenation of aromatic nitrocompounds to aromatic amines.

BACKGROUND OF THE INVENITON

[0002] Aromatic nitrocompounds are compounds where one or more nitro-groups are bound to a carbon atom in an aromatic ring. Typical aromatic nitrocompounds are e.g. nitrobenzene, nitrotoluene, nitroxylene and dinitrotoluene. Aromatic nitrocompounds can be hydrogenated to corresponding aromatic amines.

[0003] It is well known that many of the relatively high boiling aromatic amines can be prepared by liquid-phase hydrogenation of the corresponding aromatic nitrocompound in the presence of a catalyst, either with or without the use of a solvent[1]. Early catalytic hydrogenations were performed in stirred batch reactors. In this known method aromatic nitrocompound is first dissolved into a suitable solvent and pumped into a batch reactor containing the catalyst. The reactor which is equipped with a stirrer is pressurized by hydrogen gas. After the reaction is completed, the product can be separated from the solvent.

[0004] More recently batch processes have been replaced by continuous processes. A continuous liquid-phase process is illustrated by the process for diaminotoluene[2,3]. According to the process, dinitrotoluene (DNT) is catalytically hydrogenated at 150-200 bar and about 100 °C. A solution, which contains about 25 wt-% dinitrotoluene dissolved in methanol, hydrogen and Raney-nickel, is pumped through a series of reactors. Reactors are equipped with internal circulation to make the reaction more complete. After the reaction is completed, the pressure is reduced and the excess hydrogen removed in a gas-liquid separator and recycled to the beginning of the process. Catalyst is then removed and recycled, after which the solvent is distilled and recycled. The water is removed in the dehydration column. The product purity is more than 99-% pure diaminotoluene.

[0005] Low molecular weight alcohols, particularly methanol or ethanol, are the most commonly used hydrogenation solvents for hydrogenation of aromatic nitrocompounds. Other solvents, like acetic acid, ammonia, benzene, glycerol, ethylene glycol, hydrochloric acid, sulfuric acid or water can be used.

[0006] It is well known that the solubility of hydrogen into liquid-like solvents is extremely small. Due to the this low hydrogen solubility and slow transfer to the catalyst surface where the reaction product is formed, the reaction in liquid-phase is relatively slow, and continuous reactors could not always be used effectively. Several mechanical solutions have been introduced. One solution is spray column, where the solvent, nitroaromatic compound and catalyst are sprayed with the hydrogen gas.

[0007] It is known that aromatic nitrocompounds can be hydrogenated in vapor phase. In this method vaporized nitroaromatic compound and hydrogen gas are flowing through the catalyst bed forming the product. The reaction is usually very fast and high conversions are obtained with a single pass. This method is continuous and in principle simple. A method for producing aniline from nitrobenzene in trickle-bed reactor is described in literature[4]. Nitrobenzene is first vaporized and mixed with a 200 % excess of hydrogen gas. Hot gaseous mixture is flowing upward into the reduction chamber containing the copper-silica catalyst. The reaction is very fast at 270 °C and 2-3 bar. After leaving the reactor, the reaction mixture containing aniline, hydrogen and water is cooled. Excess hydrogen is first removed after which water and aniline are separated. Finally aniline is purified to a 99 % product

[0008] Catalytic hydrogenation of aromatic nitrocompounds to aromatic amines can be done in the vapor phase, provided that the boiling point of the compound is low enough and the starting material and the product are thermally stabile. These limitations mean that only relatively simple aliphatic and aromatic nitrocompounds, such as nitrobenzene and nitroxylene, can be hydrogenated in the vapor phase.

DESCRIPTION OF THE INVENTION

[0009] The present invention is based upon the discovery that aromatic nitrocompounds can be hydrogenated in the presence of a hydrogenating catalyst in CO_2 which is in supercritical or near-critical state. The aromatic nitrocompound and hydrogen gas are dissolved into the supercritical or near-critical state solvent. The resulting homogenous mixture which is in supercritical or near-critical state is brought into contact with the catalyst, and the reaction product, the aromatic amine is formed. The hydrogen concentration of the homogenous mixture can be chosen almost freely and it is not any more a restricting factor in the reaction. With the assistance of this invention a decisive improvement on previously mentioned process limitations in prior art are obtained.

[0010] The word supecritical refers to the state of the solvent. For example carbon dioxide is in supercritical state when its temperature is above 31.1 °C and simultaneously the pressure is above 73.8 bar. Supercritical fluids exhibit both liquid- and gas-like properties, such as liquid-like density and gas-like viscosity. The diffusivity of supercritical fluids is between the values of gases and liquids. Gas-like properties are considered to be beneficial in reaction chemistry due to enhanced mass transfer.

[0011] A particularly important property of supercritical fluids is, that they are almost completely misciple with all kind of gases, including hydrogen gas. This means that when the solvent is in supercritical state the hydrogen gas needed to reduce the aromatic nitrocompound to aromatic amine can be easily mixed with the solvent. In the reactors where the reaction is carried out in the vapor phase, the nitroaromatic compound is vaporized and mixed with hydrogen gas, which efficiently removes the mass transfer limitations encountered in liquid phase systems.

[0012] However, relatively high temperatures, i.e. 300-475 °C, are often needed in the vapor phase systems. In this invention complete miscibility of the nitroaromatic compound and hydrogen is obtained at significantly lower temperatures, i.e. 30-150 °C.

[0013] This invention makes possible the construction of more simple and more efficient reactors for nitroaromatic amine production. Applying the supercritical solvent can also simplify the overall process, for example separation and purification of the product. The supercritical solvent, being usually a pressurized gas, can be relatively easily separated from the product by simply depressurising the solvent mixture. The reaction can be carried out in batch reactors, but obviously continuous reactor systems are preferable in industrial practice.

[0014] Carbon dioxide is environmentally acceptable, non-toxic, non-flammable, relatively inexpensive, non-corrosive and easily available. Carbon dioxide is used in fire fighting to extinguish the flames. Carbon dioxide can act both as a solvent and a safe gas in the hydrogenation processes. Low molecular weight hydrocarbons, such as ethane and propane, are chemically stable against hydrogenation, which means that higher hydrogenation temperatures than in case of carbon dioxide can be applied.

[0015] It is well known that the character of supercritical solvent can be enhanced by addition of a modifier like short chain alcohols or esters.

[0016] The invention is described in detail in the following with the aid of embodiment examples.

Example 1. Reduction of methyl-p-nitrobenzoate in carbon dioxide with Pd-containing catalyst

[0017] 0.5 g methyl-p-nitrobenzoate (mp. 94-96 °C) and 0.057 g catalyst were weighted and placed into the batch reactor (40 mL), after which the reactor was closed. The catalyst used was palladium on polyolefinfiber. The batch reactor was purged with carbon dioxide to remove the entrapped air, and was heated to 42 °C. The system was then charged with carbon dioxide and hydrogen gases, so that the total pressure was 180 bar and hydrogen partial pressure was 15 bar. Pressurized reaction mixture was magnetically mixed for 30 minutes, after which the mixer was turned off and the reaction vessel was rapidly cooled and depressurized. The catalyst was then separated from the product. The product was analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography, and was noted to be almost pure methyl-p-aminobenzoate. The purity was over 95 %.

Example 2. Reduction of methyl-p-nitrobenzoate in carbon dioxide with Ni-containing catalyst

[0018] Using procedures similar to example 1., methyl-p-nitrobenzoate was hydrogenated. The catalyst was nickel on carbon and the reaction temperature was 100 °C. The total pressure was 80 bar and the hydrogen partial pressure was 10 bar. The product was analyzed and purity of methyl-p-aminobenzoate was over 70 %.

Example 3. Reduction of methyl-p-nitrobenzoate in carbon dioxide with Pt-containing catalyst

[0019] Using procedures similar to example 1., methyl-p-nitrobenzoate was hydrogenated. The catalyst was platinum on activated carbon and the reaction temperature was 35 °C. Small amount of methanol was used as a modifier. The total pressure was 250 bar and the hydrogen partial pressure was 40 bar. The product was analyzed and purity of methyl-p-aminobenzoate was over 90 %.

Example 4. Reduction of methyl-p-nitrobenzoate in carbon dioxide with CuO/CrO-containing catalyst

[0020] Using procedures similar to example 1., methyl-p-nitrobenzoate was hydrogenated. The catalyst contained copperoxide/chromiumoxide. The reaction temperature was 150 °C, total pressure was 300 bar and the hydrogen partial pressure was 20 bar. The product was analyzed and purity of methyl-p-aminobenzoate was over 60 %.

Example 5. Reduction of nitrobenzene in carbon dioxide with Pd-containing catalyst

[0021] 0.5 g nitrobenzene (mp. 5-7 °C) and 0.051 g catalyst were weighted and placed into the batch reactor (40 mL), after which the reactor was closed. The catalyst used was palladium on polyolefinfiber. The batch reactor was purged with carbon dioxide to remove the entrapped air, and was heated to 40 °C. The system was then charged with carbon dioxide and hydrogen gases, so that the total pressure was 200 bar and hydrogen partial pressure was 20 bar. Pressurized reaction mixture was magnetically mixed for 30 minutes, after which the mixer was turned off and the reaction vessel was rapidly cooled and depressurized. The catalyst was then separated from the product The product was analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography, and was noted to be over 90 % pure aniline.

Example 6. Reduction of 2,4-dinitrotoluene in carbon dioxide with Pd-containing catalyst

[0022] 0.5 g 2,4-dinitrotoluene (mp. 67-70 °C) and 0.27 g catalyst were weighted and placed into the batch reactor (40 mL), after which the reactor was closed. The catalyst used was palladium on polyolefinfiber. The batch reactor was purged with carbon dioxide to remove the entrapped air, and was heated to 42 'C. The system was then charged with carbon dioxide and hydrogen gases, so that the total pressure was 200 bar and hydrogen partial pressure was 19 bar. Pressurized reaction mixture was magnetically mixed for 30 minutes, after which the mixer was turned off and the reaction vessel was rapidly cooled and depressurized. The catalyst was then separated from the product. The product was analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography, and was noted to be over 90 % pure 2,4-diaminotoluene.

Example 7. Reduction of 2,4-dinitrotoluene in carbon dioxide with Ni-containing catalyst

[0023] Using procedures similar to example 1., methyl-p-nitrobenzoate was hydrogenated. The catalyst contained nickel on activated carbon. The temperature was 80 °C. Total pressure was 250 bar and hydrogen partial pressure was 30 bar. The product was analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography, and was noted to be over 85 % pure 2,4-diaminotoluene.

Example 8. Reduction of methyl-p-nitrobenzoate in propane with Pd-containing catalyst (out of the scope of the claims)

[0024] 0.5 g methyl-p-nitrobenzoate and 0.2 g catalyst are weighted and placed into a batch reactor (40 mL), after which the reactor is closed. The catalyst is palladium on carbon . The batch reactor is purged with propane to remove the entrapped air, and is heated to 105 °C. The system is then charged with propane and hydrogen gases, so that the total pressure is 75 bar and hydrogen partial pressure is 20 bar. Pressurized reaction mixture is magnetically mixed for 30 minutes, after which the mixer is turned off and the reaction vessel is rapidly cooled and depressurized. The catalyst is then separated from the product. The methyl-p-aminobenzoate product is analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography.

Example 9. Reduction of methyl-p-nitrobenzoate in ethane with Pd-containing catalyst (not within the scope of the claims)

[0025] 0.5 g methyl-p-nitrobenzoate and 0.2 g catalyst are weighted and placed into a batch reactor (40 mL), after which the reactor is closed. The catalyst is palladium on carbon. The batch reactor is purged with ethane to remove the entrapped air, and is heated to 40 °C. The system is then charged with ethane and hydrogen gases, so that the total pressure is 90 bar and hydrogen partial pressure is 20 bar Pressurized reaction mixture is magnetically mixed for 30 minutes, after which the mixer is turned off and the reaction vessel is rapidly cooled and depressurized. The catalyst is then separated from the product. The methyl-p-aminobenzoate product is analyzed with Thin Layer Chromatography (TLC) and with liquid chromatography.

[0026] This invention has above been illustrated by referring to certain favorable examples. Several modifications are possible, including starting materials, products, catalyst, pressure, temperature, time or operating mode, i.e. batch or continuous.

[0027] Literature cited

1. J.I. Kroschwitz, M. Howe-Grant, Eds.; Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., vol 2, page 489.
2. H. Dierichs and H. Holzrichter, U.S.Pat. 3 032 586 (Apr. 18, 1957)
3. H. Dierichs and H. Holzrichter; Brit.Pat. 768 111 (Feb. 13, 1957).
4. O.C. Karkalits, Jr., C.M. Vanderwaart and F.H. Megson; U.S.Pat. 2 891 094 (June 16, 1959)

Claims

1. A method for hydrogenation of aromatic nitrocompounds to aromatic amines,
Characterized in
that an aromatic nitrocompound, hydrogen gas and carbon dioxide are mixed together under elevated pressure and temperature, so that a homogenous mixture, which is at supercritical or near-critical state is formed, and the resulting homogenous mixture is brought into contact with a catalyst so that an aromatic amine product is formed.

2. A method according to claim 1,
characterized in
that the catalyst contains palladium-, platinum-, copper-, chromium- or nickel.

3. A method according to any of the previous claims,
characterized in
that methanol is used as a modifier.

Patentansprüche

1. Verfahren zur Hydrierung von aromatischen Nitroverbindungen zu aromatischen Aminen
dadurch gekennzeichnet
daß eine aromatische Nitroverbindung, Wasserstoffgas und Kohlendioxyd bei erhöhtem Druck und Temperatur zusammen gemischt werden , damit eine homogenishe in superkritische oder nahe -kritishen Zustand vorhandene Mischung gebildet wird , und daß die gebildete homogenische Mischung mit

einem Katalysator in Kontakt gebracht wird, damit ein aromatishes Amine produkt geformt wird.

2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet
daß der Katalysator Palladium Platin , Kupfer, Chrom oder Nickel enthält.

3. Verfahren nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet
daß Methanol als Modifier gebraucht wird.

Revendications

1. Procéde d'hydrogénation de composés nitro-aromatiques en amines aromatiques
caractérisé en ce que
un composé nitro-aromatique, l'hydrogène gazeux et dioxyde de carbone sont mélangés ensemble sous la pression et la température élevée pour que le mélange homogène qui est dans un état supercritique ou presque critique est formé, et le mélange homogène resulté est mise en contact avec un catalyseur pour que un produit amine aromatique est formé.

2. Procéde selon la revendication 1,
caractérisé en ce que
le catalyseur contient palladium, platine, cuivre, chrome ou nickel.

3. Méthode selon l'une quelconque des revendications précédentes,
caractérisé en ce que
méthanol est utilisé comme un modifier.