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(71) **Demandeur/Applicant:**
DEGUSSA AG, DE

(72) **Inventeurs/Inventors:**
STOCHNIOL, GUIDO, DE;
JAEGER, BERND, DE;
HAAS, THOMAS, DE;
FINKE, NORBERT, DE;
BURKHARDT, WERNER, DE;
GRUNERT, JUERGEN, DE

(74) **Agent:** MARKS & CLERK

(54) Titre : PROCEDE D'HYDROGENATION D'UNE AMINE AROMATIQUE EN PRESENCE D'UN CATALYSEUR SUPPORTE A BASE RUTHENIUM

(54) Title: PROCESS FOR HYDROGENATING AN AROMATIC AMINE IN THE PRESENCE OF A SUPPORTED RUTHENIUM CATALYST

(57) **Abrégé/Abstract:**

The invention relates to a process for hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus with hydrogen in the presence of a supported catalyst that contains ruthenium as active metal. The catalyst support of the catalyst to be used according to the invention has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of the catalyst support is formed by macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm. The process is suitable in particular for hydrogenating methylenedianiline to form bis(p-aminocyclohexyl)methane having a trans-trans isomeric component of 15 - 25%.

Process for hydrogenating an aromatic amine in the presence of a supported ruthenium catalyst

Abstract:

The invention relates to a process for hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus with hydrogen in the presence of a supported catalyst that contains ruthenium as active metal. The catalyst support of the catalyst to be used according to the invention has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of the catalyst support is formed by macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm.

The process is suitable in particular for hydrogenating methylenedianiline to form bis(p-aminocyclohexyl)methane having a trans-trans isomeric component of 15 - 25%.

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Process for hydrogenating an aromatic amine in the presence of a supported ruthenium catalyst

Description:

The invention relates to a process for hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus, wherein the hydrogenation with hydrogen takes place in the presence of a supported catalyst containing ruthenium as active metal. The catalyst to be used in the process according to the invention contains a catalyst support having a special combination of properties. The invention relates particularly to a process for hydrogenating methylenedianiline (MDA) to form bis(p-aminocyclohexyl)methane (PACM) having a content of the trans-trans isomers thereof in the range of, in particular, 15 to 25%.

The cycloaliphatic amines obtainable in the catalytic hydrogenation of aromatic amines, such as unsubstituted or substituted cyclohexyl amines and dicyclohexyl amines, are used in the preparation of polyamide and polyurethane resins, as hardeners for epoxy resins and also as raw materials for the preparation of elastic and rubber additives and also corrosion inhibitors.

It is known to prepare cycloaliphatic amines containing one or more amino groups by catalytic hydrogenation of the corresponding mononuclear or polynuclear aromatic amines containing one or more amino groups and optionally further substituents. Such amines are hydrogenated to form the corresponding cycloaliphatic amines, as emerges from numerous documents, often using supported catalysts.

Thus, in the process in accordance with US Patent 2,606,925, bis(4-aminophenyl)methane, designated below in simplified form as methylenedianiline or MDA, is hydrogenated in the presence of a ruthenium supported catalyst, active carbon, aluminium oxide and kieselguhr being named as support, to form bis(4-aminocyclohexyl)methane, denoted below in simplified form as bis(p-aminocyclohexyl)methane or PACM. In this process, PACM takes the form of the cis-cis, cis-trans and trans-trans isomers. Hydrogenation temperatures above 150°C or prolonged reaction times during the hydration result in an increased proportion of the trans-trans isomers. No indications can be found in this document of whether and in what way the selection of the catalyst or catalyst support influences the isomer distribution.

In the effort to obtain the thermodynamically more stable trans-trans isomer of PACM, the hydrogenation in accordance with US Patents 3,155,724 and 3,347,917 is performed using a ruthenium supported catalyst in the presence of ammonia. The generic hydrogenation can also be improved, in accordance with US Patent 3,914,307, in that the reaction mixture to be hydrogenated additionally contains a polyheterocyclic amine as cocatalyst. No indications can be found in the last-mentioned documents about the isomeric ratio in the case of the hydrogenation of polynuclear aromatic amines such as MDA to form PACM and also about any influence of the properties of the support material.

US Patent 5,360,934 teaches the generic method, but a rhodium-containing supported catalyst is used. Ruthenium may also be present as active metal. According to the teaching of said document, the catalyst activity depends to an appreciable extent on the modification of the aluminium oxide used as support. According to this document, catalysts containing delta-, theta- and kapa-aluminium oxide as support material are more active than a catalyst containing commercial gamma-aluminium oxide as support material.

In accordance with EP 0 066 211 A1, dianilinomethane can be converted into PACM having a trans-trans isomeric PACM component in the range from 15 to 40 wt. %, in particular 18.5 to 23.5 wt. % by performing the hydrogenation in the presence of a support-free ruthenium catalyst. Disadvantages of this process are the high hydrogenation pressure necessary and the high reaction temperature and, furthermore, the greater effort expended on separating the ruthenium catalyst from the reaction mixture.

In accordance with EP Patent 0 324 190, PACM containing the above-mentioned low trans-trans isomeric component can be obtained by hydrogenating MDA in the presence of a support-bound ruthenium catalyst. The hydrogenation takes place at 100 to 190°C and a pressure of 5 to 35 MPa, in which process, although the temperature was in the lower temperature range in the exemplary embodiments, the hydrogen pressure at 30 MPa was in the upper part of the above-mentioned pressure range. The support material of the catalyst used in this process is characterized by a BET surface area range of 70 to 280 m²/g and a mean pore diameter d_p of 1 to 32 nm; the penetration depth of the ruthenium is at least 50 µm, in particular 100 to 300 µm; the ruthenium content is specified as 0.1 to 5 wt. %, in particular 0.5 to 3 wt. %. A disadvantage of this process is the high hydrogen hydrogenation pressure still necessary in practice.

In the process in accordance with EP 0 813 906 A2, organic compounds, including also aromatic compounds in which at least one amino group is bound to an aromatic nucleus, can be hydrogenated using a ruthenium supported catalyst. In addition to ruthenium, the catalyst may contain as active metal other metals from the first, seventh or eighth subgroup of the periodic system. In contrast to the support material of EP Patent 0 324 190 considered above, the support material has, in this case, a BET surface area of not more than 30 m²/g and a mean pore diameter of at least 50 nm. The catalyst used in this case is characterized, in addition, by a ratio of the surface area of the active metal and the surface area of the catalyst support of less than 0.05. The macroporous support materials having a mean pore diameter of preferably 500 nm to approximately 50 µm are preferably aluminium oxide and zirconium oxide. Details on the hydrogenation of MDA to form PACM are not to be found in this document. In particular, the hydrogenation of aromatic compounds, such as 4-alkalyl-substituted phenols results predominantly in trans cycloaliphatic compounds. In contrast thereto, the inventors of the present application undertook the task of converting substituted aromatic amines into cycloaliphatic amines having a low trans component.

A similar process to that of EP 0 813 906 A2 is taught by EP 0 814 098 A2: the support material for the support-bound ruthenium hydrogenation catalyst for hydrogenating aromatic amines to cycloaliphatic amines used here are those materials 10 to 50% whose pore volume is formed by macropores having a pore diameter in the range from 50 nm to 10,000 nm and 50 to 90% by mesopores having a pore diameter in the range from 2 to 50 nm. The BET surface area of the support is specified as 50 to 500 m²/g, in particular 200 to 350 m²/g. The ratio of the surface of the active metal and of the support is said to be less than 0.3, in particular less than 0.1. Information about the activity of such catalysts and also the isomeric ratio in the case of the hydrogenation of MDA to form PACM cannot be found in this document. However, reference is also made here to the predominant formation of the trans isomers with reference to the hydrogenation of 4-substituted phenols.

Finally, EP 0 873 300 B1 proposes performing the hydrogenation of aromatic amines such as bis(p-aminophenyl)methane, with a catalyst containing support-bound ruthenium as active metal, the support having a mean pore diameter of at least 0.1 µm, in particular at least 0.5 µm and a surface area of not more than 15 m^2/g, preferably 0.05 to 5 m^2/g. Cycloaliphatic amines can be obtained by this process with high selectivity and without the formation of deamination products or partially hydrogenated dimerization products. References to the trans-trans isomeric component cannot be found in this document.

As is disclosed in a publication by G.F. Allen (Chem. Ind. (Dekker) (1988), 33 Catal. Org. Reakt., 323 - 338), the trans-trans isomeric PACM component increases with increasing conversion of metylhenediamine. The two above-mentioned processes relate, however, to the obtaining of a high conversion.

Finally, EP 0 639 403 A2 teaches that bis(p-aminocyclohexyl)methane can be produced by hydrogenation of methylenedianiline in an advantageous way with a ruthenium-containing or rhodium-containing supported catalyst, the layer thickness of the active metals on the support being 5 to 150 µm, preferably 10 to 80 µm. The support material is a calcined and superficially rehydrated transition argillaceous earth having a specified pH. The support has a BET surface area of at least 70 m²/g and an open porosity of at least 0.1 ml/g. References to the pore distribution cannot be found in said document. An advantage of this process is that, even after a prolonged operating time, the proportion of trans-trans PACM isomer is in the range from about 20 to 25%.

Disadvantages of this process are, however, the increased effort in establishing an equilibrium pH, the high expenditure on equipment in order to be able to apply the high hydrogen pressure (300 bar) mentioned in the examples and the limited selection of supports.

In accordance with the process disclosed in DE 199 42 813, PACM with a low trans-trans isomer component can be obtained in an advantageous way at a moderate temperature of 50 to below 130°C and a moderate hydrogen pressure of 3 to 10 MPa using a ruthenium supported catalyst bound to titanium dioxide or aluminium oxide. The specific surface area of the titanium dioxide used particularly preferably is in the range from greater than 20 m²/g to less than 70 m²/g. A disadvantage of this process is the high ruthenium content of the supported catalyst necessary. References to pore structure/distribution cannot be found in said document.

The object of the present invention is to disclose a further process for the hydrogenation of aromatic amines in the presence of a ruthenium-containing supported catalyst by which the desired cycloaliphatic amines can be obtained with higher selectivity. A further object of the invention relates to the provision of a further process for preparing bis(p-aminocyclohexyl)methane by catalytic hydrogenation of methylenedianiline, in which process the trans-trans isomeric component of the PACM should be less than 30%, in particular 15 to 25%. A further object relates to continuing to obtain a low trans-trans component despite a high conversion. In accordance with a further object, the catalyst used in the process should have a long working life and the isomer distribution should remain substantially unaltered even after a prolonged operating time.

As the further description reveals, these and further objects can be achieved by the process according to the invention.

A process was accordingly found for hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus, comprising reaction of the aromatic amine with hydrogen in the presence of a supported catalyst containing ruthenium alone as the active metal or together with at least one metal of the first, seventh or eighth subgroups of the periodic system in an amount of 0.01 to 20 wt. %, in particular 0.2 to 3 wt. % of active metals, based on the supported catalyst, applied to a support, characterized in that the catalyst support has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of the catalyst support are macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm.

The subclaims relate to preferred embodiments of the process according to the invention.

In regard to the prior art considered in detail above, in particular to EP 0 814 098 A2, it was surprising that a catalyst support having a specific surface area in the range from greater than 30 m^2/g to less than 70 m^2/g is particularly effective in the generic process if more than 50% of the pore volume is formed by macropores and less than 50% of the pore volume is formed by mesopores. It is consequently not the BET surface area alone or the pore distribution alone that is important, but the combination of these two features. The inventive combination of properties of the support material is also surprising because, in EP 0 324 190 B considered above, for a BET surface area of at least 70 m^2/g, the pore volume should substantially be formed exclusively by mesopores having a mean pore diameter of 1 to 32 nm. Finally, the catalyst to be used in the process in accordance with the present invention differs in a fundamental way from the catalyst mentioned in EP 0 813 906 A2 because, although the catalyst support in the predisclosed process is macroporous, the BET surface area should, however, be not more than 30 m^2/g and preferably not more than 15 m^2/g. The ratio of the surface area of the active metal and of the catalyst support is in the range from 0.01 to 0.5, in particular 0.03 to 0.3. Surprisingly, a low surface area ratio of the active metal, determined by CO chemisorption, and of the catalyst support, determined by BET, of 0.03 to 0.06 in the case of the catalyst to be used according to the invention also results in a high catalyst activity under mild hydrogenation conditions.

Aromatic amines:

Aromatic amines in which at least one amino group is bound to an aromatic nucleus can be hydrogenated to form the corresponding cycloaliphatic compounds by the process according to the invention. In this connection, the aromatic compounds may be mononuclear or polynuclear aromatic compounds. Preferably, the aromatic compounds are aromatic amines or diamines or triamines. The aromatic amines may be substituted on the aromatic nucleus or nuclei or/and on the amino group, for example by one or more alkyl and/or alkoxy radicals, preferably C_{1-20}-alkyl and/or C_{1-20}-alkoxy radicals. Particularly preferred substituents are C_{1-10}-alkyl radicals, in particular methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl radicals. Among the alkoxy radicals, the C_{1-8}-alkoxy radicals, in particular methoxy, ethoxy, propoxy and butoxy, are preferred. The aromatic nucleus or nuclei and also the alkyl and alkoxy radicals may optionally be substituted by halogen atoms, in particular fluorine atoms or other suitable inert or hydrogenable substituents.

The aromatic amine in which at least one amino group is bound to an aromatic nucleus may also have a plurality of aromatic nuclei that are linked by means of a bivalent hydrocarbon radical, such as a methylene group or ethylene group. The linking radical may have one or more alkyl substituents, in particular C_{1-20}-alkyl radicals, preferably one or more methyl, ethyl, n-propyl or isopropyl, n-butyl or sec-butyl or tert-butyl radicals.

Particularly preferred aromatic amines are aniline, naphtylamine, bis(p-aminophenyl)methane, and also isomers thereof, that is to say 2,4′- and 2,2′-diaminodiphenylmethane, bis(p-aminophenyl)amines, 2,2-bis(p-aminophenyl)propane, in which case one or both aromatic nuclei may have a further amino group and/or a C_1- to C_3-alkyl or alkoxy group.

Catalysts:

The supported catalysts to be used according to the invention can be prepared industrially by applying ruthenium and optionally at least one metal of the first, seventh or eighth subgroup to a suitable support. The application can be achieved by impregnating the support in aqueous metal salt solutions, such as ruthenium salt solutions, by spraying suitable metal salt solutions onto the support or by other suitable processes. Suitable as salts for preparing the ruthenium salt solutions and also solutions of metal salts of elements of the first, seventh or eighth subgroup are the nitrates, nitrosyl nitrates, halides, carbonates, carboxylates, acetylacetonates, chlorine complexes, nitro complexes or amine complexes of the corresponding metals; preferred are nitrates and nitrosyl nitrates.

In the case of catalysts that contain yet further metals in addition to ruthenium applied to the support, the metal salts or metal salt solutions can be applied simultaneously or consecutively.

The supports coated or impregnated with a ruthenium salt or additionally further metal salt solutions are dried, preferably at temperatures between 100°C and 150°C, and optionally calcined at temperatures between 200°C and 600°C. The coated supports are then activated by treating the coated supports in a gas stream containing free hydrogen at temperatures between 30 and 600°C, preferably between 150 and 400°C. The gas stream is preferably composed of 50 to 100 vol. % of H_2 and 0 to 50 vol. % of N_2.

If yet one or more other metals of the first, seventh or eighth subgroup are applied to the supports in addition to ruthenium, and the application takes place consecutively, the support may be dried after every application or impregnation at temperatures between 100 and 150°C and optionally calcined at temperatures between 200 and 600°C. In this connection, the order in which the metal salt solutions are applied may be chosen as desired.

In accordance with a preferred embodiment, the support is coated by spraying a metal salt solution on at elevated temperature, in particular above 50°C and, particularly preferably, at 80 to 150°C so that the solvent is at least partly evaporated even during the coating and the penetration depth of the catalytically active metal is limited. Preferably, the penetration depth is in the range from 5 to 250 µm, in particular 10 to 150 µm and, particularly preferably, 50 to 120 µm.

The ruthenium salt solution and, optionally, further metal salt solutions are applied to the support or supports in an amount such that 0.01 to 20 wt. %, based on the total weight of the catalyst, of ruthenium and, optionally, other metals of the first, seventh or eighth subgroup are applied to the support. Preferably, the amount of active metal is 0.2 to 15 wt. %, in particular about 0.2 to 3 wt. %, the ruthenium content expediently exceeding the content of the other metals.

Support materials:

The support materials of the catalysts to be used according to the invention have a specific BET surface area (determined with N_2 in accordance with DIN 66131) in the range from greater than 30 m²/g and less than 70 m²/g.

The support contains macropores having a pore diameter of greater than 50 nm. The diameter of the macropores is, in particular, in the range from 50 to 50,000 nm, in many cases, however, in the range from 50 to 10,000 nm. If the support also comprises mesopores, these are understood to be pores in the range from 2 to 50 nm. At least 50% of the pore volume is formed by macropores and less than 50% by mesopores. Preferred supports contain macropores in an amount of 55 to 85% of the pore volume and 15 to 45% of the pore volume is occupied by mesopores. In particularly preferred supports, mesopores occupy about 25 to 45% of the pore volume and macropores the rest of the pore volume. If present, micropores having a pore diameter of less than 2 nm are present only in an amount of less than 10% of the pore volume, in particular less than 1%.

The modification of the support may be uniform or mixed so that the pore distribution may be monomodal, bimodal or trimodal.

In principle, all the known support materials can be used for hydrogenation catalysts provided they have the claimed BET surface, pore size and pore distribution. Oxidic, silicatic and nitridic supports are suitable and, specifically, with a single-phase or multiphase crystalline or X-ray amorphic or mixed structure.

The supports may furthermore be modified in a known way with alkali-metal or/and alkaline-earth-metal compounds and/or with metals of the lanthanide series.

Exemplary supports are oxides from the series comprising Al_2O_2, TiO_2, ZrO_2, SiO_2, MgO and ZnO, furthermore mixed oxides such as spinels, for example $MgAl_2O_4$. Aluminosilicates and active carbons are also suitable if these supports have the claimed combination of properties. Particularly preferred are the oxides Al_2O_3 and TiO_2.

Hydrogenation conditions:

The hydrogenation is performed at a temperature in the range from 20 to 250°C, in particular at below 200°C, and an effective H_2 partial pressure in the range from about 1 to 30 MPa, preferably below 10 MPa, in a continuously operated or batch-operated suspension-type or fixed-bed hydrogenation reactor. The activity of the catalysts according to the invention make it possible to perform the hydrogenation under mild conditions, in particular at a temperature in the range from 50 to 150°C, in particular 70 to 120°C and an H_2 pressure in the range from 3 to 10 MPa, with the result that industrially less expensive reactors can be used, which increases the cost-effectiveness of the process.

The hydrogenation can be performed in the presence or absence of a suitable solvent. Preferably, a solvent is present and, specifically, in an amount of about 10 to 90 wt. %, based on the solution of the aromatic amine to be hydrogenated.

Suitable solvents are, for example, primary, secondary and tertiary monohydric or polyhydric alcohols, such as methanol, ethanol, n-propanol and isopropanol, n-, sec-, and tert-butanol, ethylene glycol, ethylene glycol mono(C_1-C_4)alkyl ethers; linear ethers, such as ethylene glycol di(C_1-C_3)alkyl ethers; cyclic ethers, such as tetrahydrofuran and dioxane; alkanes, such as n-alkanes and isoalkanes containing 4 to 12 C atoms, for example n-pentane, n-hexane and isooctane, and cyclic alkanes, such as cyclohexane and decalin.

The hydrogenation can also be performed in the presence of ammonia or a primary, secondary or tertiary amine or a polycyclic amine having a bridged N atom. Expediently, path-finding experiments ensure that no undesirable isomerization occurs among those chosen in the case of PACM, that is to say in the direction of a higher trans-trans component.

The solvent may also be the hydrogenation product itself, that is to say a cycloaliphatic amine.

For continuous hydrogenation, a fixed-bed reactor is preferred. The fixed-bed reactor can be operated as a bubble reactor but a trickle-bed mode is preferred. Preferably, a trickle-bed reactor having an LHSV value in the range from 0.1 to 5 h^{-1} (=l of the aromatic amines to be hydrogenated per l fixed bed catalyst and hour). In accordance with a particularly preferred embodiment of the process according to the invention, a multitube fixed-bed reactor is used and it is operated in the trickle-bed mode.

The present invention furthermore relates to a support-bound catalyst suitable for the process according to the invention. The subject matter is consequently a supported catalyst that contains, as active metal, ruthenium alone or together with at least one metal of the first, seventh or eighth subgroup of the periodic system in an amount of 0.01 to 20 wt. % of active metals, based on the supported catalyst applied to a support for the purpose of hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus, characterized in that the catalyst support has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of the catalyst support is macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm. Said catalyst can be used for other hydrogenations, for example the hydrogenation of phenols and nitriles. Preferably, the amount of ruthenium exceeds the amount of the other active metals. Preferably, the catalyst contains 0.2 to 3 wt. % of active metals, wherein at least 90% is, in particular, ruthenium. Further features and preferred embodiments are disclosed in connection with the process according to the invention.

<u>Examples:</u>

Preparation of the catalyst:

<u>Example 1:</u>

An aluminium oxide moulding (extrudate, d = 3 mm) having a BET surface area of approximately 33 m^2/g and a bimodal pore distribution having a pore volume of 0.41 ml/g, in which substantially no pores were found that had a diameter of 2 to 50 nm, but 100% of the pore volume comprised macropores having a diameter in the range from 50 to

10,000 nm, was coated with an aqueous ruthenium(III) nitrate solution at approximately 90 to 100°C by spraying the catalyst solution onto the moving support material, in which process water simultaneously evaporated. The catalyst solution had a concentration of 5% metal, based on the weight of the solution. The support coated in this way was heated at a temperature of 120 to 180°C and then reduced with a mixture of 50% H_2 and 50% N_2 at 200°C for 4 h. The catalyst prepared in this way contained 3 wt. % ruthenium, based on the total weight of the catalyst. The ruthenium penetration depth was 70-90 µm. The ratio of the ruthenium surface determined by CO chemisorption to the surface of the uncoated support material determined by BET was about 0.05. The aluminium oxide moulding was substantially composed of alpha- and gamma-Al_2O_3 (approximately 18 wt. % SiO_2 and approximately 2 wt. % alkali-metal and alkaline-earth oxides, Fe_2O_3 and Ti_2O.

Example 2:

An aluminium oxide moulding (extrudate, d = 3 mm) of similar composition to that of the support in Example 1 having a BET surface area of approximately 32 m^2/g, trimodal pore distribution and a pore volume of 0.58 ml/g was impregnated analagously as in Example 1. The pore volume of the support material resulted from 31% pores having a pore diameter of from 2 to 50 nm, 44% pores 50 to 10,000 nm and 25% pores having a pore diameter of greater than 10% nm to 5 µm. The catalyst prepared in this way contained, as Example in 1, 3 wt. % ruthenium and the penetration depth was 70 to 90 µm.

Example 3:

An aluminium oxide moulding (extrudate, d = 3 mm) having a surface area of approximately 54 m^2/g had, with a trimodal pore distribution, a pore volume of 0.77 ml/g. 40% of the pore volume resulted from pores having a diameter of 2 to 50 nm, 60% of pores having a pore diameter of 50 to 10,000 nm. The impregnation of the support, and calcination and reduction of the catalyst took place in the same way as in Example 1. The catalyst prepared in this way contained 3 wt. % ruthenium, based on the total weight of the catalyst. The penetration depth was 70 to 90 µm. The aluminium oxide moulding used comprised the alpha-, theta- and gamma-Al_2O_3 modifications.

Example 4:

An aluminium oxide moulding composed of spheres having a diameter of 2-4 mm and having a BET surface area of approximately 35 m^2/g had, with a monomodal pore distribution, a pore volume of 0.5 ml/g. 42% of the pore volume was formed by mesopores (2 to 50 nm) and 58% by macropores (50 to 10,000 nm). The support material comprised the theta- and gamma-Al_2O_3 modifications. The impregnation, calcining and reduction took place in the same way as in Example 1. The support-bound ruthenium catalyst obtained in this way contained 3 wt. % ruthenium, based on the total weight of the catalyst. The ruthenium penetration depth was 80 to 120 µm.

Comparison Example 1:

A titanium dioxide moulding (extrudate, d = 2 mm) substantially composed of a mixture of rutile and anatase having a BET surface area of 45 m^2/g had, with a monomodal pore distribution, a pore volume of 0.35 ml/g. The pore volume was formed by 100% of mesopores (2 to 50 nm). The moulding was impregnated analogously as in Example 1, but the drying took place at 150 to 160°C and the subsequent reduction took place at 180°C within 4 h. The catalyst prepared in this way contained 3 wt. % ruthenium, based on the total weight of the catalyst. The penetration depth was 90 to 120 µm.

Comparison Example 2:

An aluminium oxide moulding (extrudate, d = 1.2 mm) composed substantially of gamma-Al_2O_3 having a BET surface area of 220 m^2/g had a pore volume of 0.65 ml/g, where 95% of the pore volume was formed by mesopores (2 to 50 nm) and 5% of the pore volume was formed by macropores (50 to 10,000 nm). The support was impregnated with an aqueous ruthenium(III) nitrate solution at room temperature. The catalyst solution had a concentration of 5% metal, based on the weight of the solution. The impregnated support was heated at a temperature of 150 to 160°C and then reduced with a mixture of 50% H_2 and 50% N_2 at 180°C for 4 h. The catalyst prepared in this way contained 5 wt. % of ruthenium, based on the total weight of the catalyst. The penetration depth was 600 µm.

Performance of the hydrogenation reaction

Examples 5 to 8 and Comparison Examples 3 and 4.

In each case, 30 ml of a ruthenium supported catalyst in accordance with one of Examples 1 to 4 or Comparison Examples 1 to 2 were loaded into a tubular reactor heated by an external jacket; the reactor was equipped with a precipitation device. The fixed-bed reactor was first subjected to hydrogen at 90°C and then loaded with a solution composed of 20 vol % of 4,4'-methylenedianiline and 80 vol % tetrahydrofuran. Hydrogenation was carried out at a hydrogen partial pressure of 8 MPa. The catalyst loading during this trickle-bed procedure was 0.43 [h^{-1}]. During the trickling, the temperature was raised to 110°C.

The table below shows operating data and results, including the reaction temperature, the use of a catalyst according to the invention or not according to the invention, the 4,4'-methylenedianiline (MDA) conversion, the MDA conversion per g Ru/h, and also the content of the trans-trans isomeric component. The percentages relate to area percentages determined by gas chromatography.

The extraordinary activity of the Ru supported catalysts to be used according to the invention emerges from the results of the examples according to the invention. If the catalysts according to the invention are used, PACM is produced that has a trans-trans isomeric component in the range of about 15-25%.

Table:

Ex. No.	Catalyst	Hydrogenation temperature (°C)	MDA conversion (%)	% MDA conversion / g Ru·h	g PACM / g Ru·h	PACM trans-trans-isomers (%)
E 5/1	E 1	102	97.4	170	3.3	18
/2	E 1	105	99.4	174	3.5	20
/3	E 1	110	99.8	175	3.6	25
E 6/1	E 2	94	99.8	169	3.0	15
/2	E 2	102	100	170	3.7	21
E 7	E 3	100	99	184	4.5	16
E 8/1	E 4	98	94.2	149	3.9	22
CE 3/1	CE 1	100	96.3	113	2.0	22
/2	CE 1	105	98.4	115	2.3	25
CE 4	CE 2	94	93	89	1.8	20

Patent Claims

1. A process for hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus, comprising reaction of the aromatic amine with hydrogen in the presence of a supported catalyst containing ruthenium alone as active metal or together with at least one metal of the first, seventh or eighth subgroups of the periodic system in an amount of 0.01 to 20 wt % of active metals, based on the supported catalyst, applied to a support, characterized in that the catalyst support has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of the catalyst support are macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm.

2. Process according to Claim 1, characterized in that the active metal applied to the catalyst has a penetration depth into the support in the range of 20 to 500 µm, in particular 25 to 250 µm.

3. Process according to Claim 1 or 2, characterized in that the ratio of the surfaces of the active metal, determined by CO pulse chemisorption, and of the catalyst support, determined by BET, is greater than 0.01, in particular 0.03 to 0.3.

4. Process according to any of Claims 1 to 3, characterized in that the support material is selected from the series comprising crystalline and amorphous oxides and silicates, in particular selected from the series comprising Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, ZnO and aluminosilicates.

5. Process according to any of Claims 1 to 4, characterized in that the catalayst support has a BET surface in the range from 32 to 67 m^2/g, the penetration depth of the active metals is in the range from 50 to 200 µm and the

amount of Ru is in the range from 0.2 to 3 wt. %, based on the catalyst, and at least 55% of the pore volume of the catalyst support is formed by macropores and less than 45% by mesopores.

6. Method according to any of Claims 1 to 5, characterized in that a 4,4′-diaminodiphenyl(C_1 to C_4)alkane and/or a 2,4′- oder 2,2‘ isomer thereof, in particular 4,4′-diaminodiphenylmethane or an isomer thereof is hydrogenated.

7. Process according to any of Claims 1 to 6, characterized in that the hydrogenation is performed at a temperature in the range from 20 to 200 °C, in particular 50 to 150°C, and a hydrogen partial pressure in the range from 3 to 30 MPa, in particular 3 to 10 MPa.

8. Process according to any of Claims 1 to 7, characterized in that the hydrogenation is performed in a fixed-bed reactor, in particular in a multitube fixed-bed reactor, in the trickle-bed mode.

9. Process according to any of Claims 1 to 8, characterized in that a supported catalyst is used whose active metal ruthenium was applied to a support by spraying the support with a dilute ruthenium salt solution, in particular a ruthenium nitrosyl nitrate solution at a temperature of at least 80°C and then drying.

10. Supported catalyst that contains, as active metal, ruthenium alone or together with at least one metal of the first, seventh or eighth subgroup of the periodic system in an amount of 0.01 to 20 wt % of active metals, based on the supported catalyst applied to a support for the purpose of hydrogenating an aromatic amine that has at least one amino group bound to an aromatic nucleus, characterized in that the catalyst support has a BET surface area in the range from greater than 30 m^2/g to less than 70 m^2/g and more than 50% of the pore volume of

the catalyst support are macropores having a pore diameter of greater than 50 nm and less than 50% are mesopores having a pore diameter of 2 to 50 nm.