(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 May 2020 (22.05.2020)

(10) International Publication Number
WO 2020/098937 A1

(51) International Patent Classification:
B01J 37/02 (2006.01) *C07C 209/14* (2006.01)
B01J 23/89 (2006.01) *C07C 211/01* (2006.01)

(21) International Application Number: PCT/EP2018/081274

(22) International Filing Date: 14 November 2018 (14.11.2018)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants: RHODIA OPERATIONS [FR/FR]; 25 rue de Clichy, 75009 Paris (FR). **LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE** [FR/FR]; 3, rue Michel-Ange, 75794 Paris Cedex 16 (FR). **ECOLE NORMALE SUPERIEURE DE LYON** [FR/FR]; 15 Parvis René Descartes, 69342 LYON 7ème (FR). **UNIVERSITE LILLE 1 - SCIENCES ET TECHNOLOGIES** [FR/FR]; Cité Scientifique, 59655 Villeneuve d'Ascq (FR). **ECOLE CENTRALE DE LILLE** [FR/FR]; Cité Scientifique, CS 20048, 59651 Villeneuve d'Ascq Cedex (FR). **UNIVERSITE D'ARTOIS** [FR/FR]; 9, rue du Temple, BP 10665, 62030 Arras Cedex (FR).

(72) Inventors: IBÁÑEZ ABAD, Javier; c/ Barcelona 60-64, 7°B, 08210 Barberà del Vallès (ES). **PAUL, Sébastien**; 58 rue du Rieu, 59158 Thun Saint-Amand (FR). **PERA-TITUS, Marc**; 199 Mincheng Road, block 19, Appart 304, SHANGHAI, 201100 (CN).

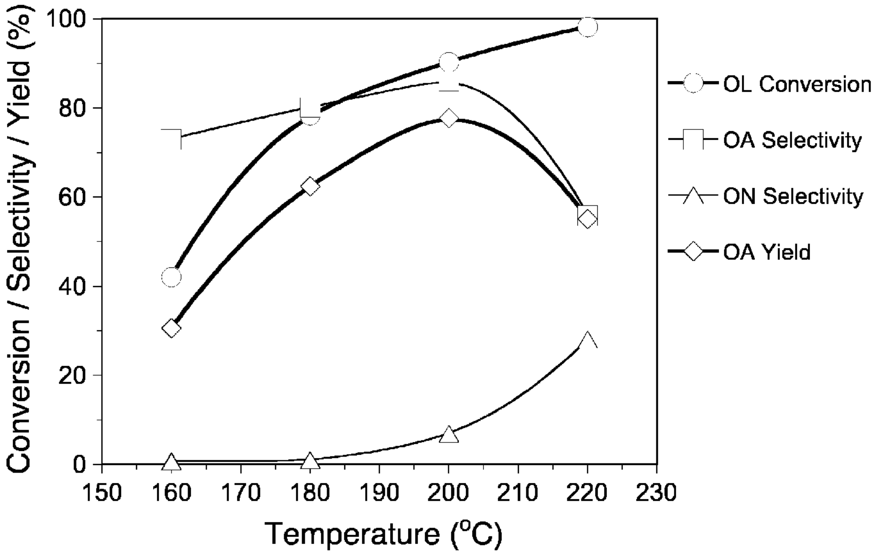
(74) Agent: DELENNE, Marc; 40, rue de la Haie Coq, F-93306 Aubervilliers Cedex (FR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

(54) Title: METHOD FOR PRODUCING AN AMINE

Figure 5



(57) Abstract: The invention relates to a method for producing an amine by reacting an alcohol, aldehyde and/or ketone with hydrogen and nitrogen-containing compound in the presence of a silver and/or ruthenium promoted cobalt catalyst. The nitrogen-containing compound is selected from ammonia, primary amines and secondary amines.

WO 2020/098937 A1

[Continued on next page]

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to non-prejudicial disclosures or exceptions to lack of novelty (Rule 4.17(v))*

Published:

— *with international search report (Art. 21(3))*

Method for producing an amine

TECHNICAL FIELD OF THE INVENTION

The invention relates to a method for producing an amine by reacting an alcohol, aldehyde and/or ketone with hydrogen and a nitrogen-containing compound in the presence of a silver and/or ruthenium promoted cobalt catalyst. The nitrogen-containing compound is selected from ammonia, primary amines and secondary amines.

BACKGROUND

The catalytic amination of alcohols is a well-known process. By this process hydroxy-containing compounds, aldehydes, and ketones can be aminated by reacting said compounds with ammonia, primary amines or secondary amines in a continuous or batch-wise process in the presence of hydrogen gas and a hydrogenation-dehydrogenation catalyst. All hydrogen atoms on an ammonium or amine are potentially replaceable by the alkyl radical of the hydroxy-containing compound, aldehyde and ketone. The reaction product will therefore usually be a mixture of primary, secondary and tertiary amines. However, the most desirable products are such containing mainly primary amino groups. Therefore, there is an interest in catalysts which, not only have high activity in the amination reaction, but also show high selectivity towards the desired primary amine.

Various catalysts have been used to promote the process and most of them are based on nickel and/or cobalt. In order to improve the selectivity in respect to the product mix and to increase the reaction rate, a large number of promoters has been used, such as compounds of copper, magnesium, chromium, iron, and zinc. For example, DE 1950604 discloses a method for producing an amine by reacting an alcohol with ammonia or an amine in the presence of hydrogen and a catalyst which contains Co, Mn, Zn, Cr, Ag and Cu. Cobalt-containing catalysts which are promoted by ruthenium are disclosed for example in US 4,701,334, EP 0 839 574 A2 and EP 0 839 575 A2.

Nickel, palladium, platinum and cobalt supported catalysts are generally reported as efficient catalysts for the amination of aromatic and aliphatic alcohols. However, when reacting primary alcohols with ammonia a high excess of ammonia and low conversion (<10-30%) is necessary to obtain moderate to high selectivity (20-60%) towards the primary amine.

Among the aforementioned catalysts, cobalt-based catalysts supported on alumina stands out in terms of selectivity towards the primary amine, being possible to obtain a >80% selectivity at 50% alcohol conversion at non-optimized conditions. On the other hand, the catalyst lacks activity in comparison with its nickel or platinum counterparts.

Furthermore, cobalt metal is known to strongly interact with the alumina support generating inactive cobalt aluminate species. This strong metal-support interaction greatly affects the metal reducibility, and therefore its activity, by means of reducing the available metallic cobalt under reaction conditions. One known strategy to overcome this issue is to promote cobalt with noble metals.

Additionally, the reaction conditions can influence the overall conversion of the alcohol, aldehyde or ketone and in particular the selectivity of the reaction towards the desired product, in particular the primary amine. The above-cited prior art documents for example suggest to conduct the reaction under high pressure of for example 30MPa (DE 1950604) or from 8 to 40 MPa (US 4,701,434).

A further parameter is the amount of the amination agent present during the reaction. In the prior art (US 4,701,434 and DE 1950604) it is suggested to use for example ammonia as aminating agent in an excess of up to 30 moles per mole of the compound to be aminated.

The reaction between the aminating agent and the compound to be aminated is carried out in the presence of hydrogen gas. According to US 4,701,434 the quantity of hydrogen gas required is relatively small, and corresponds to a proportion of from about 0.1 to about 2 moles per mole of hydroxy. Higher proportions of hydrogen gas are said to be without any noticeable benefit.

There is still a need for further improving the known methods for the amination of alcohols, in particular with respect to high conversion and simultaneously high selectivity towards a desired amine, most especially towards primary amines.

SUMMARY OF THE INVENTION

The present inventors have found that amines, and in particular primary amines, can be produced in high yield from alcohol, aldehyde and/or ketone in the presence of hydrogen and a nitrogen-containing compound and in the presence of a silver and/or ruthenium promoted cobalt catalyst, if the reaction is conducted in the presence of a relatively high amount of hydrogen.

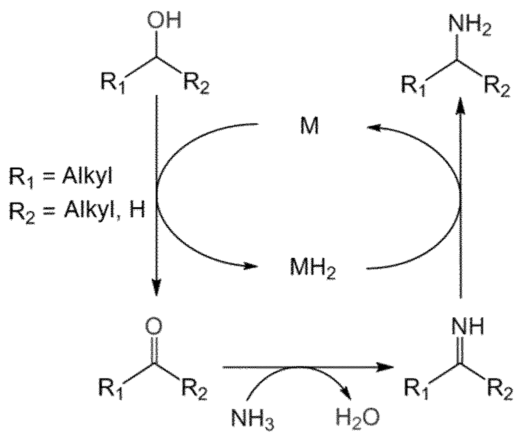
The present invention therefore relates to a method for producing an amine by reacting an alcohol, aldehyde and/or ketone with hydrogen and nitrogen-containing compound, selected from ammonia, primary amines and secondary amines, in the presence of a silver and/or ruthenium promoted cobalt catalyst, characterized in that the reaction is conducted in the presence of at least 4.5 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

The finding that an increasing amount of hydrogen in the reaction facilitates the yield of the desired amine is particularly surprising, because it was assumed in the prior art that the amount of hydrogen has no relevant influence on the reaction and it was even suggested to use a relatively small proportion of from only 0.1 to 2 moles per mole hydroxy groups.

DETAILED DESCRIPTION

The present invention relates to a method for producing an amine by reacting an alcohol, aldehyde and/or ketone with hydrogen and a nitrogen-containing compound in the presence of a catalyst. The reaction is illustrated by the following reaction scheme 1.

Scheme 1



As can be seen, the conversion of the alcohol to the corresponding amine consists of three consecutive steps:

(a) dehydrogenating the alcohol to its corresponding aldehyde or ketone,
(b) adding the aminating agent to that reaction product to form an imine (or enamine),
(c) hydrogenating the imine to the corresponding amine.

From the reaction scheme it is also evident that the catalytic reaction of the invention is not only useful for the amination of alcohols but also for the amination of aldehydes and ketones.

As it will be demonstrated by the examples below, the present inventors surprisingly found that while the relative amount of the aminating agent had no significant impact on the catalytic activity, the amount of hydrogen had a great impact on the conversion of the alcohol, aldehyde or ketone. Therefore, the method of the invention is characterized in that the reaction is conducted in the presence of at least 4.5 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated. Preferably the reaction is conducted in the presence of at least 5 moles, more preferably in the presence of at least 6 moles, 7 moles, 8 moles, 9 moles or even 10 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

If the reaction conditions in the method of the invention are selected such that the reaction is conducted as gas-phase reaction, the ratio of hydrogen to hydroxy and/or carbonyl groups to be aminated can alternatively be defined as the partial pressure of the hydrogen in the reaction mixture. In this case, the hydrogen in the reaction mixture should have a partial pressure of at least 18 % of the total pressure. For example, if the reaction is conducted at a total pressure of about 100 kPa, the hydrogen partial pressure should be at least 18 kPa. Preferred minimum partial pressures of hydrogen in the reaction mixture are at least 20 %, at least 24 %, at least 30 %, at least 36 % and preferably at least 40 % of the total pressure in the reaction mixture.

Even more surprising it was, however, also found that a further increase of the relative amount of hydrogen had a negative impact on the selectivity of the reaction. Therefore, in one embodiment of the present invention, the reaction is conducted in the presence of not more than 30 moles, preferably not more than 25 moles, more preferably not more than 20 moles and most preferably not more than 15 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated. In further embodiments the reaction is conducted in the presence of 5 to 30 moles, preferably 5 to 20 moles, more preferably of 5 to 15 moles and even more preferably of 10 to 15 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

If the reaction is conducted as gas-phase reaction, the partial pressure of the hydrogen in the reaction mixture can be not more than 80 %, preferably not more than 70 %, and most preferably not more than 60 % of the total pressure of the reaction mixture. Preferred partial pressures of the hydrogen in the reaction mixture are in the range of 18 % to 70 %, more preferably in the range of 18 % to 60 % of the total pressure of the reaction mixture.

While the catalysts used in the method of the present invention show a maximum in selectivity when the reaction is conducted in the presence of about 10 to 15 moles of hydrogen per mole of hydroxy and/or carbonyl group to be aminated it was surprisingly found that optimum conversion is obtained with different catalysts at different hydrogen concentrations. In particular, it was observed that at relatively low hydrogen concentrations the silver promoted cobalt catalyst overperforms the ruthenium promoted cobalt catalyst in terms of activity. At higher hydrogen concentrations, the ruthenium promoted cobalt catalyst showed higher activity than the silver promoted cobalt catalyst.

Therefore, in a further embodiment of the present invention, the catalyst is a silver promoted cobalt catalyst and the reaction is conducted in the presence of 4.5 to 12 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

In another embodiment the catalyst is a ruthenium promoted cobalt catalyst and the reaction is conducted in the presence of at least 6 moles, preferably of at least 9 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated. In this embodiment, the given lower limits can be combined with any of the above upper limits, such as for example 6 to 30 or 70 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

The amount of nitrogen-containing compound in the reaction mixture is not particularly limited. It is, however, preferred that the nitrogen-containing compound is present in excess in the mixture, for example, within the range of from 2 to 30 moles per mole of hydroxy and/or carbonyl groups to be aminated, preferably within the range of from 2 to 15 moles per mole, even more preferably in the range of from 2 to 10 moles per mole of hydroxy and/or carbonyl groups to be aminated.

The amount of catalyst in the reaction mixture is also not critical, but normally it will be 0.1-25%, preferably 1-15% by weight of the total amount of starting reactants in a batch-wise process.

The amination process of the invention can be carried out over a wide range of pressures. The pressure employed is dependent upon the molar ratio of the reactants, the reaction temperature, the amount of hydrogen, and the kind of operation. The pressure can be high enough to keep most of the reactants in the liquid phase in which case the pressure can for example be in the range of 8 to 40 MPa. In the method of the invention it is, however, preferred to select the pressure low enough to keep most of the reactants in the gas phase. This is because it was observed that at the high ratio of hydrogen to hydroxy and/or carbonyl groups to be aminated, the conversion and selectivity towards the desired primary amine surprisingly decreases. Therefore, in one embodiment of the invention the reaction is conducted at a total pressure in the range of 50 to 1500 kPa, preferably 100 to 1000 kPa, even more preferably 100 to 750 kPa.

The temperature at which the amination reaction of the invention is conducted is also not particularly limited. It is, however, preferred that the reaction is conducted at an elevated temperature of for example within the range of from 120 °C to 300 °C.

Usually, the conversion of the alcohol, aldehyde, and/ketone to the amine increases with the temperature. The present inventors, however, found that while the selectivity towards the primary amine also enhances while increasing the temperature, the selectivity reaches a maximum at about 200 °C and at higher temperatures the selectivity decreases. Therefore, the reaction of the invention is preferably conducted at a temperature in the range of 150 °C to 200 °C, more preferably 180 °C to 210 °C, and most preferably at about 200 °C.

The catalyst used in the amination reaction of the present invention is also not particularly limited as long as the catalyst comprises cobalt which is promoted with silver and/or ruthenium. Thus, the catalyst may comprise further metals, such as Mn, Zn, Cr, Cu, Ni, and mixtures thereof. The catalyst may also comprise further metals for promoting its activity, in particular further noble metals, such as Pt, Pd and Au.

In one embodiment, the catalyst comprises in addition to the catalytically active metals a support, in particular an inert support, such as a solid porous support. In this context the term "inert" is to be understood as defining a support which does substantially not and in particular not take part in the amination reaction of the present invention. In particular the support should not have any substantial catalytic activity for the amination reaction, preferably it should not have any catalytic activity for the amination reaction at the given reaction conditions.

The support which may be used for the catalyst in the present invention is not particularly limited and can be selected among catalyst supports known and used in the art. For example, the support can be a metal oxide, preferably a metal oxide selected from alumina, silica, titania, magnesia, zirconia, and combinations thereof. Alumina is a preferred support.

The amount of cobalt being supported on the support is not limited and can be selected by the skilled person according to the requirements. The amount of cobalt being supported on the support can be, for example, in the range of 1 to 30 wt.% or 1 to 20 wt.% of Co based on the total weight of the catalyst. The inventors, however, found that silver and ruthenium promote the cobalt catalyst to an extent that it is possible to significantly reduce the amount of cobalt comprised in the catalyst thereby nevertheless maintaining its activity. Therefore, in preferred embodiments the catalyst used in the method of the invention comprises 1 to 10 wt.% of Co, more preferably 1 to 7 wt.% of Co, even more preferably 3 to 7 wt.% of Co, such as 4 to 6 wt.% of Co, each based on the total weight of the catalyst.

It was found that silver and ruthenium significantly promote the catalytic activity of the cobalt. Surprisingly only low amounts of silver and ruthenium are required for achieving the desired effect. It was also found that ruthenium is even more effective than silver. Therefore, in one embodiment the catalyst used in the method of the invention comprises at least 0.1 wt.% of Ag, preferably at least 0.2 wt.% of Ag, more preferably at least 0.5 wt.% of Ag, even more preferably at least 1 wt.% or even at least 2 wt.% of Ag, and most preferably at least 2.5 wt.% of Ag, each based on the weight of the Co. Alternatively or additionally, preferably alternatively, the catalyst comprises at least 0.01 wt.% of Ru, preferably at least 0.02 wt.% of Ru, more preferably at least 0.1 wt.% of Ru, even more preferably at least 0.2 wt.% of Ru and most preferably at least 0.25 wt.% of Ru, each based on the weight of the Co.

The inventors furthermore found that while an increasing amount of silver or ruthenium increases the catalytic activity and the selectivity of the catalyst, there is a certain maximum amount which should not be exceeded, because at higher amounts both, activity and selectivity of the catalyst decrease. Therefore, in a preferred embodiment the catalyst comprises a maximum of 10 wt.%, preferably a maximum of 7 wt.%, more preferably a maximum of 4 wt.% and even more preferably a maximum of 3.5 wt.% of Ag, each based on the weight of the Co. Alternatively or additionally, preferably alternatively, the catalyst comprises a maximum of 10 wt.% of Ru, preferably a maximum of 7 wt.% of Ru, more preferably a maximum of 5 wt.% of Ru, and most preferably a maximum of 1 wt.% of Ru, each based on the weight of the Co.

For example, the catalyst may comprise an inert support, 1 to 20 wt.% of Co based on the total weight of the catalyst, and 0.1 to 10 wt.%, preferably 0.2 to 7 wt.% of Ag based on the weight of the Co.

In an alternative embodiment the catalyst may comprise an inert support, 3 to 7 wt.% of Co based on the total weight of the catalyst, and 0.5 to 4 wt.%, preferably 2.5 to 3.5 wt.% of Ag based on the weight of the Co.

In a further alternative embodiment the catalyst may comprise an inert support, 1 to 20 wt.% of Co based on the total weight of the catalyst, and 0.01 to 10 wt.%, preferably 0.02 to 7 wt.% of Ru based on the weight of the Co.

In a further alternative embodiment the catalyst may comprise an inert support, 3 to 7 wt.% of Co based on the total weight of the catalyst, and 0.1 to 5 wt.%, preferably 0.25 to 1 wt.% of Ru based on the weight of the Co.

While the catalyst used in the method of the invention may comprise metals other than cobalt, silver and/or ruthenium, it is preferred that the catalyst substantially consists of inert support, cobalt and the promoter selected from silver and ruthenium. In this context, "substantially consists of" means that the catalyst should not comprise any additional components, in particular metals, such as catalytically active metals, in addition to the inert support, cobalt, silver and ruthenium. Preferably, the catalyst comprises less than 10 wt.%, more preferably less than 5 wt.%, even more preferably less than 1 wt.% of metals other than those in the inert support, cobalt, silver and ruthenium. In one embodiment, the catalyst consists of inert support, cobalt and silver. In another embodiment, the catalyst consists of inert support, cobalt and ruthenium. In the last two embodiments the catalyst may nevertheless comprise traces of other elements, in particular impurities.

The method of the invention is suitable for the amination of alcohols, aldehydes and/or ketones. Single compounds or mixtures of any of these compounds can be aminated. In one embodiment of the invention the method relates to the amination of primary or secondary alcohols, preferably primary alcohols.

Alcohols which can be aminated in the method of the present invention include saturated aliphatic monohydric and polyhydric alcohols having from 1 to 30 carbon atoms, such as from 4 to 30 carbon atoms or from 6 to 30 carbon atoms, including, for example, saturated monohydric alcohols, such as methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, n-pentanol, isopentanol, neopentanol, n-hexanol, isohexanol, 2-ethyl hexanol, cyclohexanol, n-heptanol, n-octanol, 2-octanol, isooctanol, and tert-octanol, and various isomers of nonanol, decanol, hendecanol, dodecanol, tridecanol, tetradecanol, hexadecanol, and octadecanol, arachidyl alcohol, aliphatic dihydric alcohols having from two to thirty carbon atoms, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and higher polyethylene glycols, 1,2- and 1,3-propylene glycol, dipropylene glycol, tripropylene glycol and higher polypropylene glycols, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 2,3-butylene glycol, dibutylene glycol, tributylene glycol or higher polybutylene glycols, isomers of pentanediol, hexanediol, octanediol, nonanediol, decanediol, undecanediol, dodecanediol, tridecanediol, tetradecanediol, pentadecanediol, hexadecanediol, octadecanediol, eicosanediol, and trihydric and higher polyols having from three to thirty carbon atoms, such as glycerol, erythritol, pentaerythritol, sorbitol, mannitol, trimethylol ethane, trimethylol propane, heptanetriol, and decanetriol.

Further, it is possible to use aldehydes and ketones derived from the above mentioned alcohols e.g. by dehydrogenation. Suitable aldehydes are formaldehyde, acetaldehyde, propionaldehyde, butyraldehydes, cyclohexanal benzaldehyde, and aldehydes prepared by the dehydrogenation of dihydric and trihydric alcohols, monoalkylene glycol ethers, polyalkylene glycol ethers, and alkanolamines. Suitable ketones are acetone, methyl-ethyl-ketone, various isomers of pentanone and hexanone, 1-phenyl-2-propanone, acetophenone, n-butyrophenone, and benzophenone as well as ketones prepared by dehydrogenation of dihydric and trihydric alcohols, mono- and polyalkylene glycol ethers and alkanolamines.

Among phenols suitable for amination may be mentioned phenol, o-cresol, m-cresol, p-cresol, pyrocatechin, resorcinol, hydroquinone and isomers of xylenol, and among aliphatic aminoalcohols those having from two to thirty carbon atoms, such as monoethanolamine, diethanolamine, aminoethyl ethanolamine, propanolamines, butanolamines, pentanolamines, hexanolamines, heptanolamines, octanolamines, decanolamines, dodecanolamines, tetradecanolamines, hexadecanolamines, octadecanolamines, and eicosanolamines. In addition, mixtures of the above alcohols can be employed, for example, mixtures of ethylene glycol and monoethanolamine, or mixtures of alkanolamines which are obtained by reacting alkylene oxides with ammonia.

The nitrogen-containing compound used in the amination reaction of the invention is selected from ammonia, primary amines and secondary amines. The amines generally have alkyl groups of 1 to 20 carbon atoms, cycloalkyl groups of 5 to 8 carbon atoms and aryl- or arylalkyl groups of 6 to 40 carbon atoms. Examples of suitable amines are monomethylamine, dimethylamine, monoethylamine, diethylamine, n-propylamine, di-n-propylamine, iso-propylamine, di-isopropylamine, isopropylethylamine, n-butylamine, di-n-butylamine, s-butylamine, di-s-butylamine, iso-butylamine, n-pentylamine, s-pentylamine, iso-pentylamine, n-hexylamine, s-hexylamine, iso-hexylamine, cyclohexylamine, ethylenediamine, benzylamine, aniline, toluidine, piperidine, morpholine, pyrrolidine, and any combination thereof.

The amination reaction in the method of the invention may be conducted continuously or batch-wise. Conducting the reaction continuously is preferred. If the reaction is conducted batch-wise the above amounts of hydrogen and nitrogen-containing compound as well as the above pressures relate to the start of the reaction. If the reaction is conducted continuously, these parameters relate to the point where the reaction mixture enters the reactor.

The equipment used for carrying out the amination reaction of this invention can be any conventional high-temperature and high-pressure equipment adapted for batch or continuous operation. For example, in a batch process a pressure reactor vessel can be used, such as an autoclave equipped with an agitator and heating means. The method can be carried out in a continuous process, wherein the reactants in gas and liquid phase are passed under pressure over a solid catalyst bed maintained at the desired temperature. The catalyst can also be in a fluidized bed, or passed concurrently to the reaction mixture.

The catalyst used in the method of the invention can be prepared according to usual methods known in the art. For example, the support material used may be co-precipitated with cobalt salts, or this metal can be transferred to the support by impregnation with solutions of cobalt salts. Various organic and inorganic cobalt salts may be used for co-precipitation or impregnation.

Examples for suitable salts are cobalt nitrate, cobalt acetate, cobalt formate, and cobalt acetyl acetonate. Cobalt chloride may be used, but this salt is not decomposed by heating in air. Instead it can be transferred into metal by heating in hydrogen gas. Another method of deposing metals on the support is using a cobalt carbonyl gas and decomposing it on the surface of the support to extremely finely divide this metal.

After the support being impregnated with the desired amount of cobalt salt, it is dried and then calcined to decompose the salt into metal oxide. This can be accomplished by heating the catalyst first gently and, if desired, under reduced pressure to evaporate the impregnating solvent, then in a stream of air raising the temperature to 300°C to 600°C, depending on the decomposition temperature of the salt used. It is possible to transfer the oxide formed into metal prior to ruthenium or silver treatment by reacting the catalyst intermediate with hydrogen gas at elevated temperature.

The ruthenium and silver treatment of the cobalt catalyst is performed by impregnating it with a solution in water or in an organic solvent of the chosen ruthenium salt or silver salt and drying at elevated temperature in a stream of inert gas, air or hydrogen. The impregnation may be performed by spraying the solution evenly onto the catalyst, or adsorbing the ruthenium or silver compound from the diluted solution to the surface of the coated support, or wetting the catalyst with ruthenium or silver solution and evaporating the solvent.

The ruthenium or silver salt is then reduced to ruthenium or silver metal by hearting the catalyst at about 150 °C to 200 °C for 0.5 to 3 hours in a stream of hydrogen gas. Then the temperature is risen, preferably to 300 °C to 600 °C, still in the stream of hydrogen, and the temperature is kept at that level until the desired degree of reduction is reached.

The above described sequence of first precipitating the cobalt and secondly precipitating the ruthenium or silver can be conducted in reversed order by first precipitating the ruthenium or silver and then precipitating the cobalt or both metals can be co-precipitated.

In one embodiment of the present invention, the catalyst is a silver promoted cobalt catalyst which is prepared by first precipitating silver or its precursor and subsequently precipitating cobalt or its precursor. In another embodiment, the catalyst is a ruthenium promoted cobalt catalyst which is prepared by co-precipitation of cobalt and ruthenium or their precursors.

In the attached Figures

Figure 1 shows catalytic results on the amination of n-octanol with ammonia for Ag-Co catalysts (1a) and Ru-Co catalysts (1b),

Figure 2 shows the effect of the total pressure on the amination of n-octanol with ammonia,

Figure 3 shows the effect of hydrogen and ammonia partial pressures in the catalytic activity of Co, Ag-Co and Ru-Co catalysts,

Figure 4 shows the effect of hydrogen and ammonia partial pressures on the primary amine yield of Co, Ag-Co and Ru-Co catalysts, and

Figure 5 shows the effect of temperature on the amination of n-octanol with ammonia over Ag-Co.

The following Examples are given by way of non-limiting illustration of the present invention.

EXAMPLES

Materials

γ-Al_2O_3 (Sasol SCCa-5/170, 150 m^2/g) was used as a support. Cobalt nitrate hexahydrate (Sinopharm Chemical Reagent Co.), silver nitrate (Sinopharm Chemical Reagent Co.) and ruthenium (III) nitrosyl nitrate (1.5 wt.% solution, J&K chemicals) were used as precursors.

Ammonia (<99%, Air Liquide) and n-Octanol (<99%, J&K Chemicals) were used on the catalytic tests.

Synthesis of catalysts

The different catalysts were prepared by the incipient wetness method. The metal precursor was dissolved in just enough distilled water to fill the γ-Al_2O_3 pores (0.52 g H_2O / 1 g γ-Al_2O_3). The precursor solution was added dropwise to the support while mixing with a stirring bar. After adding the precursor solution, the mixture was left impregnating during 2 h at room temperature. After impregnation the sample was dried at 120°C for 12 h and calcined at 400°C during 2 h, at a heating rate of 3°C/min. The promoter was co-impregnated or sequentially impregnated as indicated:

Ag-Co / Al_2O_3

On a first step, 5 g of γ-Al_2O_3 were impregnated dropwise with 2.62 g of an 8.67 mg/g silver nitrate solution in distilled water. The mixture was left for impregnation for 2 h, dried and calcined as above indicated.

1.3 g of cobalt nitrate hexahydrate were dissolved in 2.6 g of water and impregnated onto the recovered sample. The mixture was further left for impregnation during 2 h, dried and calcined as before indicated.

The resulting catalyst had a 5 wt.% of cobalt content, and was promoted with a 3% (Ag atoms / Co atoms) of silver.

Ru-Co / Al_2O_3

1.3 g of cobalt nitrate hexahydrate and 96.3 mg of ruthenium(III) nitrosyl nitrate solution (1.5 w/v %) were dissolved in 2.5 g of water and impregnated dropwise onto 5 g of γ-Al_2O_3. The mixture was left for impregnation during 2 h, dried and calcined as before indicated.

The resulting catalyst had a 5 wt.% of cobalt content, and was promoted with a 0.3% (Ru atoms / Co atoms) of ruthenium.

Further catalysts with different metal contents as described below were prepared by the same methods.

Amination tests

The catalysts were tested in the gas-phase amination of 1-octanol with ammonia in a fixed-bed reactor at 180 °C and, if not indicated otherwise, at 101 kPa total pressure using a feed flowrate of $0.76\ mL \cdot h^{-1}$. The NH_3:H_2:N_2:1-octanol molar ratio in the gas mixture fed to the reactor was set as indicated below. Before the reaction, the catalysts were reduced at different temperatures according to their corresponding H_2-TPR profiles. The recovered liquid samples were analyzed offline using a GC (Shimadzu GC-2010 Plus) equipped with a 30 m x 0.25 mm x 0.25 μm Zebron ZB-5MS column and a FID detector. The column was temperature-programmed with a $3\ K.min^{-1}$ initial ramp from 626 °C to 646 °C followed by a $50\ K.min^{-1}$ ramp to 846 °C and holding this temperature for 3 min.

Example 1

In this Example the effect of the promoter loading on the amination reaction was examined. The results are shown in Figures 1a and 1b. The catalysts tested contained 12 wt.% Co and 5 wt.% Co, respectively, without any promoting metal (Reference Examples). It can be seen that the decrease in the amount of cobalt results in a decrease of both, conversion and selectivity towards the desired primary amine (designated as RNH2). In the reactions according to the invention the cobalt catalysts were additionally promoted by Ag and Ru, respectively. Each of the promoted catalysts contained 5 wt.% of Co based on the total weight of the catalyst and the amount of Ag or Ru indicated in Figure 1a and 1b each relates to the weight of the Co.

From the data in Figures 1a and 1b it can be seen that promoting the Co catalyst with Ag or Ru increases both, conversion and selectivity of the catalyst towards the primary amine. The increase can be to an extent that conversion and selectivity of the promoted catalyst comprising 5 wt.% of cobalt is about the same as a non-promoted catalyst comprising 12 wt.% of cobalt. Furthermore, the maximum for conversion and selectivity is observed at 3 wt.% of Ag and 0.3 wt.% of Ru.

Example 2

The effect of the total pressure on the amination of n-octanol with ammonia over Ag-Co (5 wt.% of Co on γ-Al_2O_3 promoted with 0.28 wt.% of Ag based on the weight of the Co) was tested using the following reaction conditions: 180 °C; P = 1-15 bar; NH_3:H_2:ROH (mole%) = 9:6:1; N_2 balance; $WHSV_{ROH} = 2.1\ h^{-1}$. The results are shown in Figure 2 wherein S. means selectivity.

The results demonstrate that both, conversion and selectivity towards the primary amines decreases with increasing pressure.

Example 3

In this Example the effect of the promoter on the catalytic activity at different hydrogen and ammonia pressures was tested.

The catalysts, together with a non-promoted 5 wt.% Co/Al_2O_3 sample were tested at different partial pressures of hydrogen and ammonia. The results for the catalytic activity can be seen in Figure 3.

While the pressure of ammonia did not significantly impact the catalytic activity, the pressure of hydrogen had a great impact on the conversion. Increasing the hydrogen pressure enhanced the catalytic activity for the 3 samples, with differences on the trend they followed.

At low hydrogen pressure (12-30 kPa) the silver promoted sample overperformed the ruthenium doped sample and the benchmark cobalt sample in terms of activity. At higher pressures the CoRu catalyst showed higher activity than the Ag-Co catalyst.

Example 4

In this Example the effect of the promoter on the selectivity at different hydrogen and ammonia pressures was tested.

The catalysts together with a non-promoted 5 wt.% Co/Al_2O_3 sample were tested at different partial pressures of hydrogen and ammonia. The results for the yield towards n-octylamine can be seen in Figure 4.

As it would be expected, increasing the ammonia partial pressure led to a higher yield of the primary amine. On the other hand, pressures above 30 kPa of hydrogen had a negative impact on the selectivity for all 3 catalysts, especially at low ammonia partial pressures.

Example 5

The effect of the temperature on the properties of the Ag-Co catalyst for n-octanol amination with NH_3 was surveyed in the range 160-220 °C using an $ROH:H_2:NH_3$ molar ratio of 1:6:21 and balance N_2. Figure 5 plots the results obtained. The n-octanol conversion increased from 40% at 160 °C to reach almost full conversion at 220 °C. Interestingly, the n-octylamine selectivity is also enhanced with the temperature, attaining 87% at 200 °C. The n-octylamine yield reaches a value as high as 78%.

CLAIMS

1. Method for producing an amine by reacting an alcohol, aldehyde and/or ketone with hydrogen and a nitrogen-containing compound, selected from ammonia, primary amines and secondary amines, in the presence of a silver and/or ruthenium promoted cobalt catalyst, characterized in that the reaction is conducted in the presence of at least 4.5 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

2. Method according to claim 1, wherein the reaction is conducted in the presence of 5 to 30 moles, preferably 5 to 20 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

3. Method according to claim 1 or 2, wherein the reaction is conducted at a total pressure in the range of 50 to 1500 kPa, preferably 100 to 1000 kPa, even more preferably 100 to 750 kPa.

4. Method according to claim 1 or 3, wherein the catalyst is a silver promoted cobalt catalyst and the reaction is conducted in the presence of 4.5 to 12 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

5. Method according to any of claims 1 to 3, wherein the catalyst is a ruthenium promoted cobalt catalyst and the reaction is conducted in the presence of at least 6 moles, preferably of at least 9 moles of hydrogen per mole of hydroxy and/or carbonyl groups to be aminated.

6. Method according to any of claims 1 to 4, wherein the catalyst comprises an inert support, 1 to 20 wt.% of Co based on the total weight of the catalyst, and 0.1 to 10 wt.%, preferably 0.2 to 7 wt.% of Ag based on the weight of the Co.

7. Method according to claim 6, wherein the catalyst comprises an inert support, 3 to 7 wt.% of Co based on the total weight of the catalyst, and 0.5 to 4 wt.%, preferably 2.5 to 3.5 wt.% of Ag based on the weight of the Co.

8. Method according to any of claims 1 to 3 or 5, wherein the catalyst comprises an inert support, 1 to 20 wt.% of Co based on the total weight of the catalyst, and 0.01 to 10 wt.%, preferably 0.02 to 7 wt.% of Ru based on the weight of the Co.

9. Method according to claim 8, wherein the catalyst comprises an inert support, 3 to 7 wt.% of Co based on the total weight of the catalyst, and 0.1 to 5 wt.%, preferably 0.25 to 1 wt.% of Ru based on the weight of the Co.

10. Method according to any of claims 6 to 9, wherein the support is a metal oxide, preferably a metal oxide selected from alumina, silica, titania, magnesia, zirconia, and combinations of any of these oxides.

11. Method according to any of the preceding claims, wherein the reaction is conducted at a temperature in the range of 150 °C to 250 °C, preferably 180 °C to 210 °C, most preferably at about 200 °C.

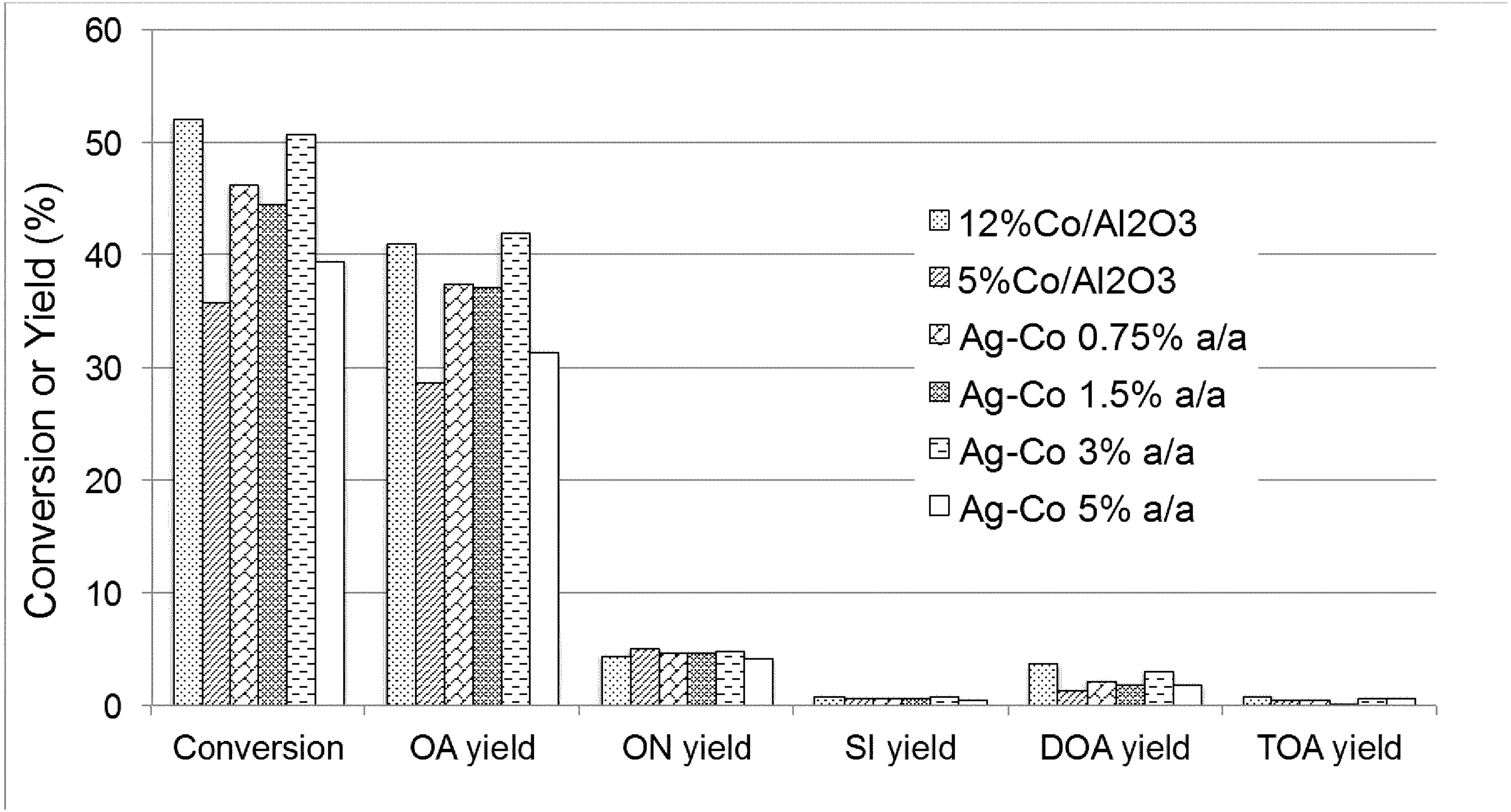
12. Method according to any of the preceding claims, wherein a primary or secondary alcohol, preferably a primary alcohol, is aminated.

13. Method according to any of the preceding claims, wherein the nitrogen-containing compound is selected from ammonia, monoalkylamines and dialkylamines, preferably from ammonia, monomethylamine, dimethylamine, monoethylamine, diethylamine, n-propylamine, di-n-propylamine, iso-propylamine, di-isopropylamine, isopropylethylamine, n-butylamine, di-n-butylamine, s-butylamine, di-s-butylamine, iso-butylamine, n-pentylamine, s-pentylamine, iso-pentylamine, n-hexylamine, s-hexylamine, iso-hexylamine, cyclohexylamine, ethylenediamine, benzylamine, aniline, toluidine, piperidine, morpholine, pyrrolidine and any combination thereof.

14. Method according to any of the preceding claims, wherein the catalyst substantially consists of inert support, cobalt and the promotor selected from silver and ruthenium.

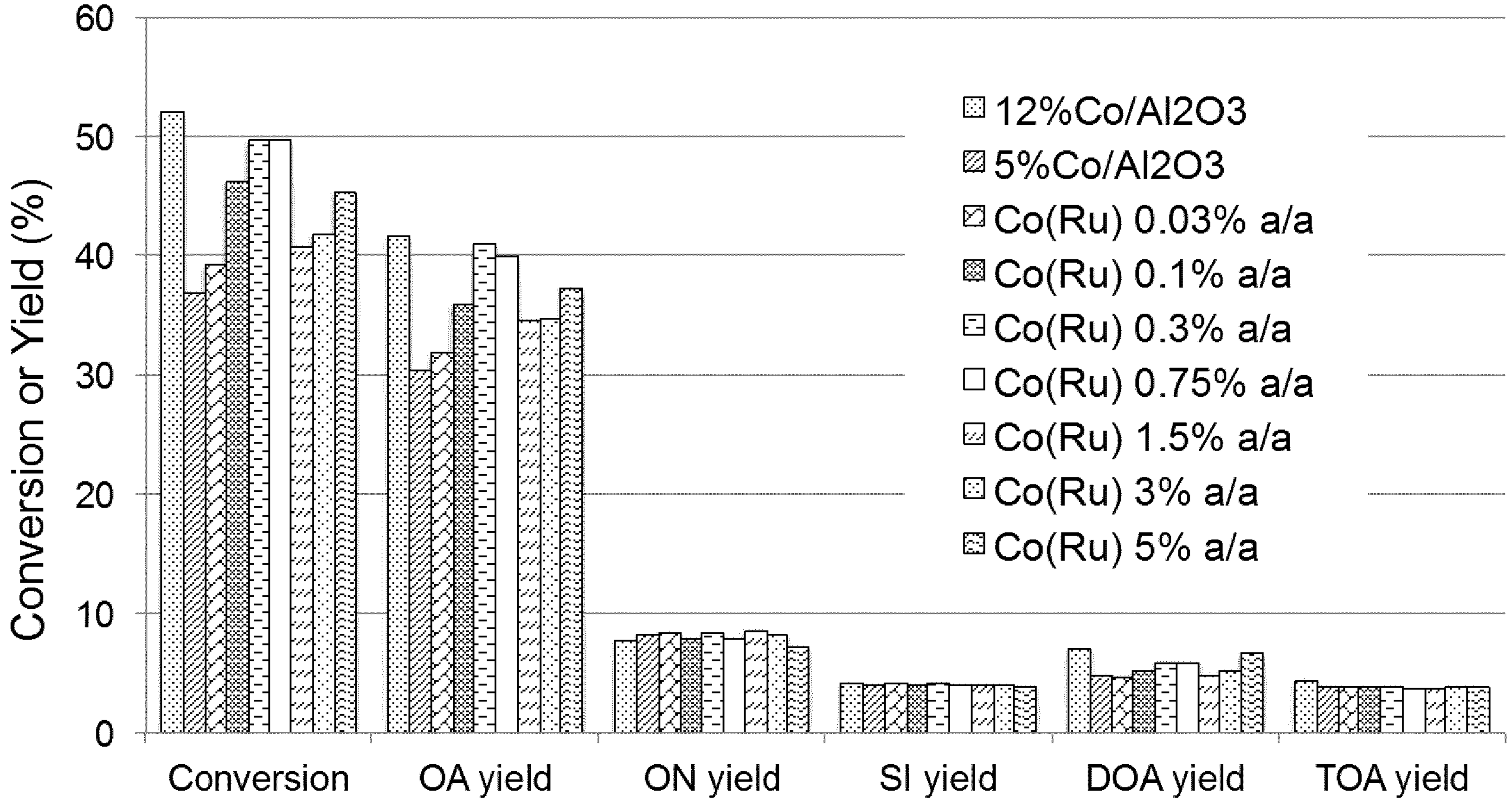
15. Method according to any of the preceding claims, wherein the reaction is conducted continuously.

Figure 1a



Reaction conditions: 180 °C, 9 equiv. NH_3, 3.4 equiv. H_2, 1.2 mL/h 1-octanol, 510 mg catalyst

Figure 1b



Reaction conditions: 180 °C, 9 equiv. NH_3, 3.4 equiv. H_2, 1.2 mL/h 1-octanol, 510 mg catalyst

Figure 2

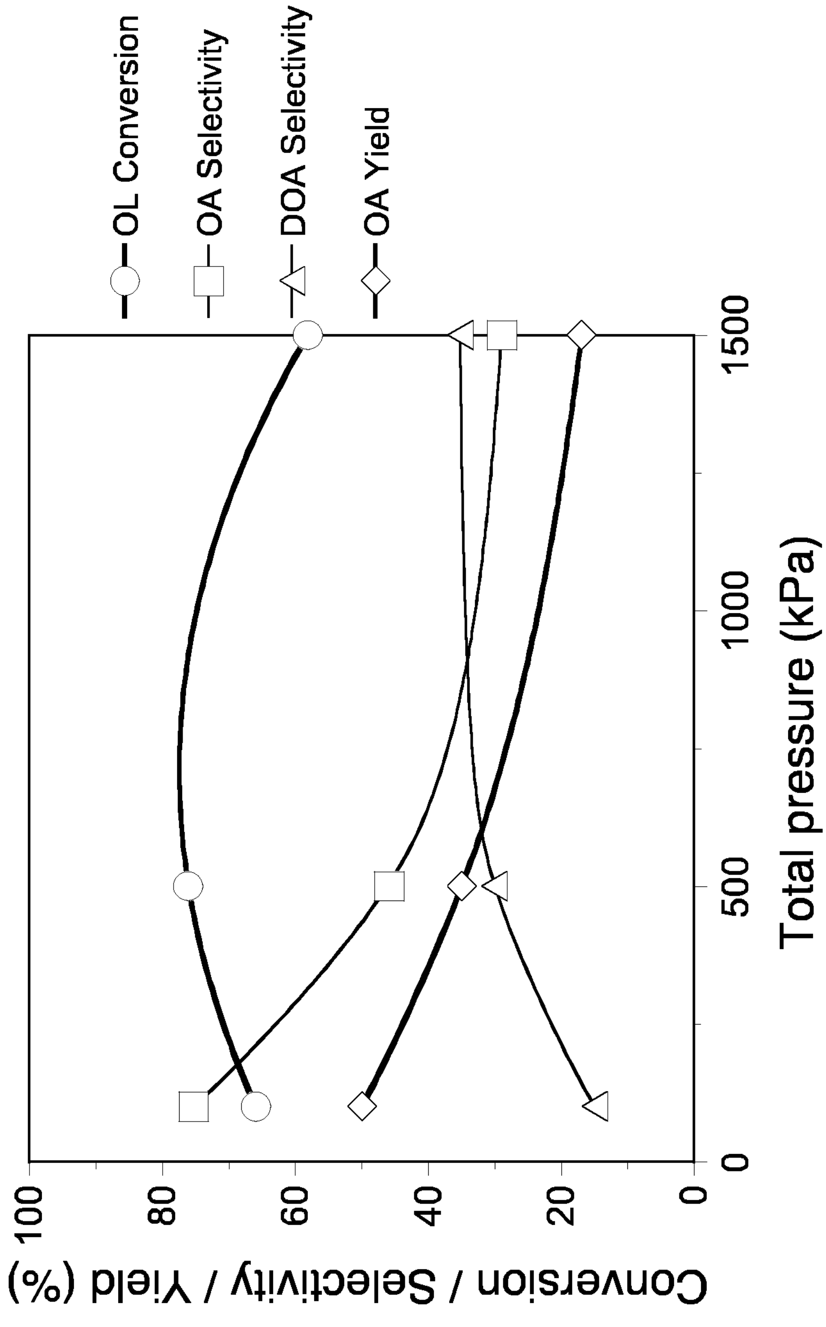

Conversion / Selectivity / Yield (%)
0
20
40
60
80
100
Total pressure (kPa)
0
500
1000
1500
OL Conversion
OA Selectivity
DOA Selectivity
OA Yield

Figure 3

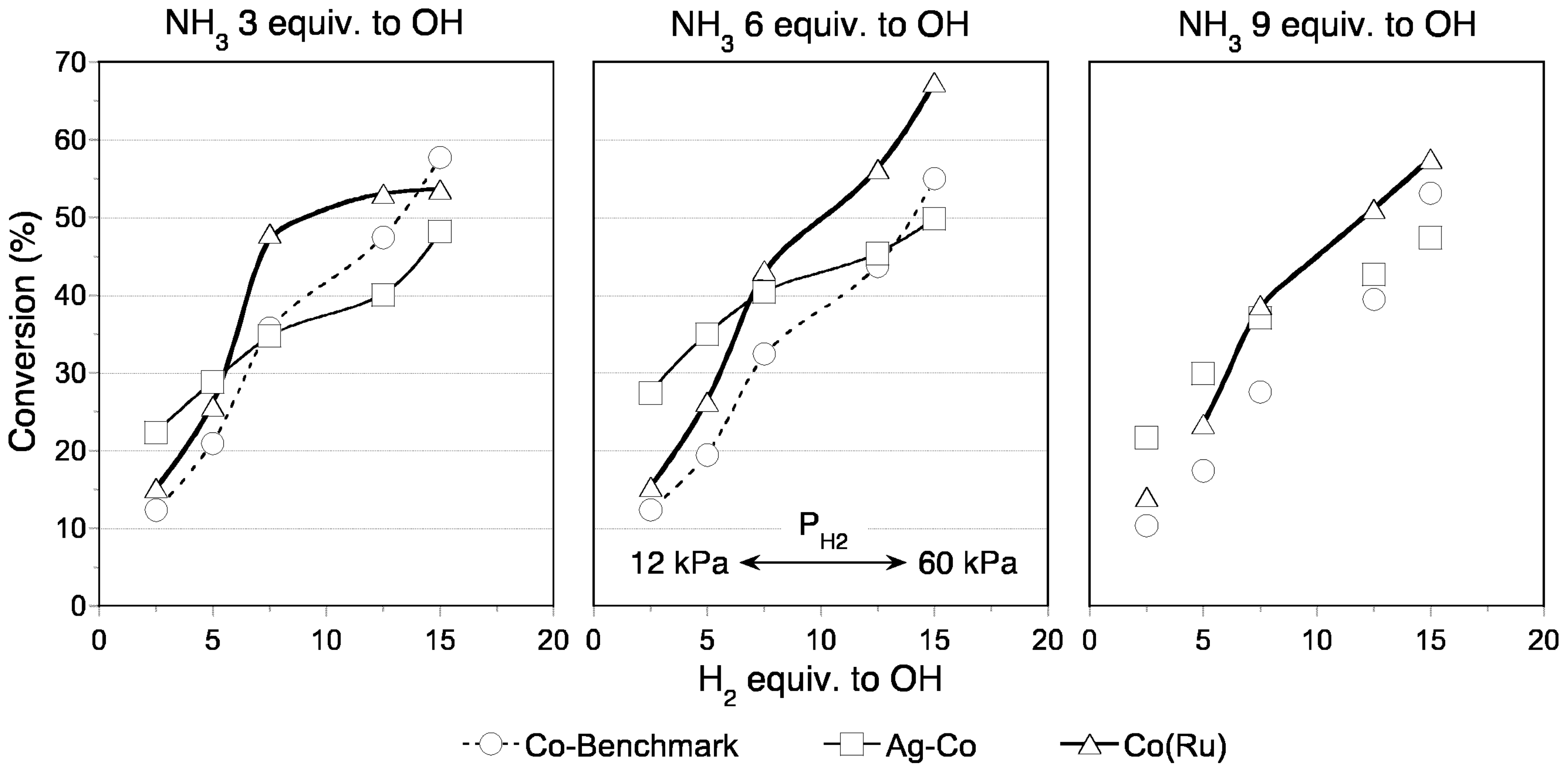

NH_3 3 equiv. to OH
NH_3 6 equiv. to OH
NH_3 9 equiv. to OH
Conversion (%)
0
10
20
30
40
50
60
70
0
5
10
15
20
H_2 equiv. to OH
P_{H2}
12 kPa
60 kPa
Co-Benchmark
Ag-Co
Co(Ru)

Figure 4

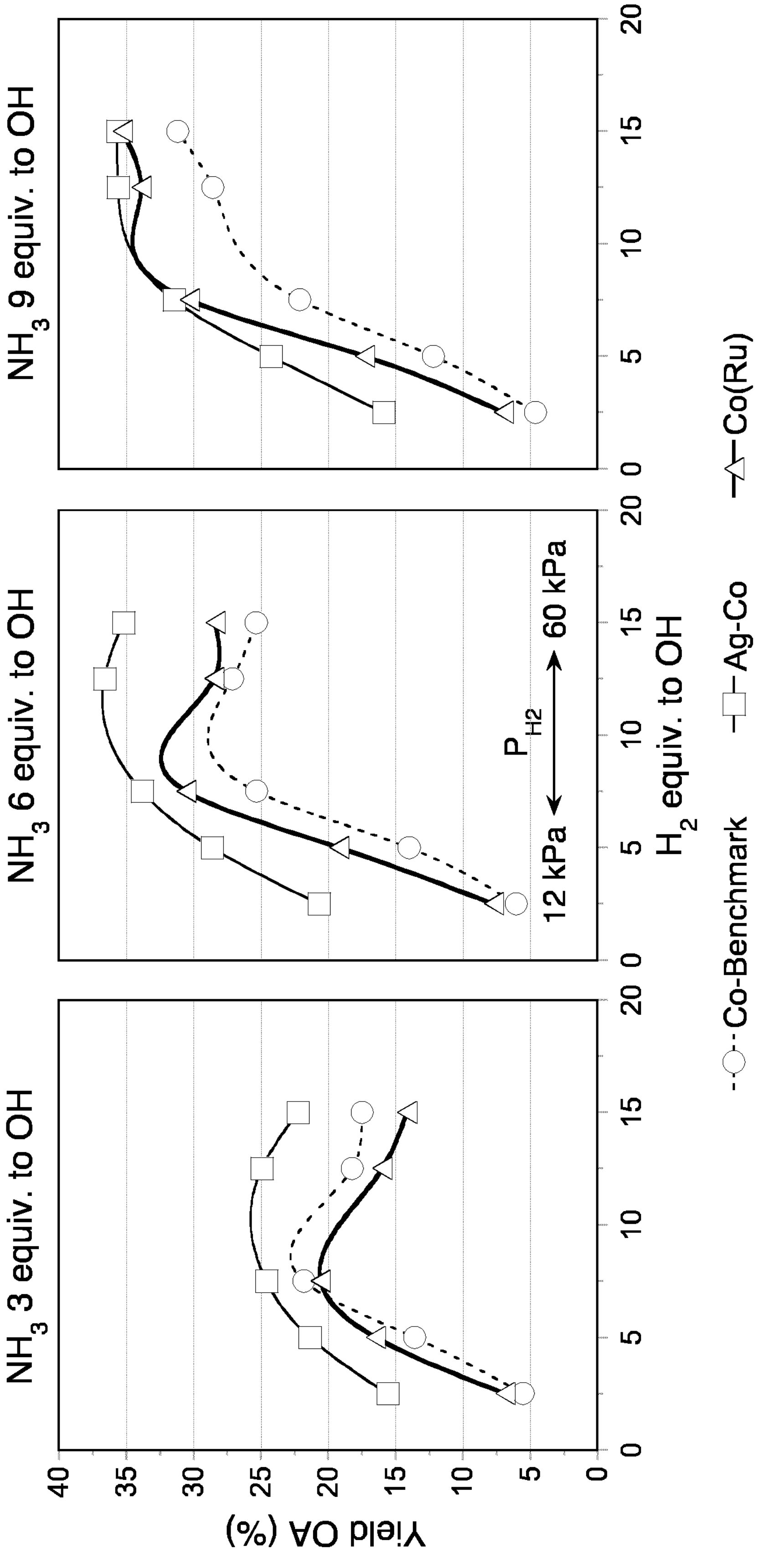
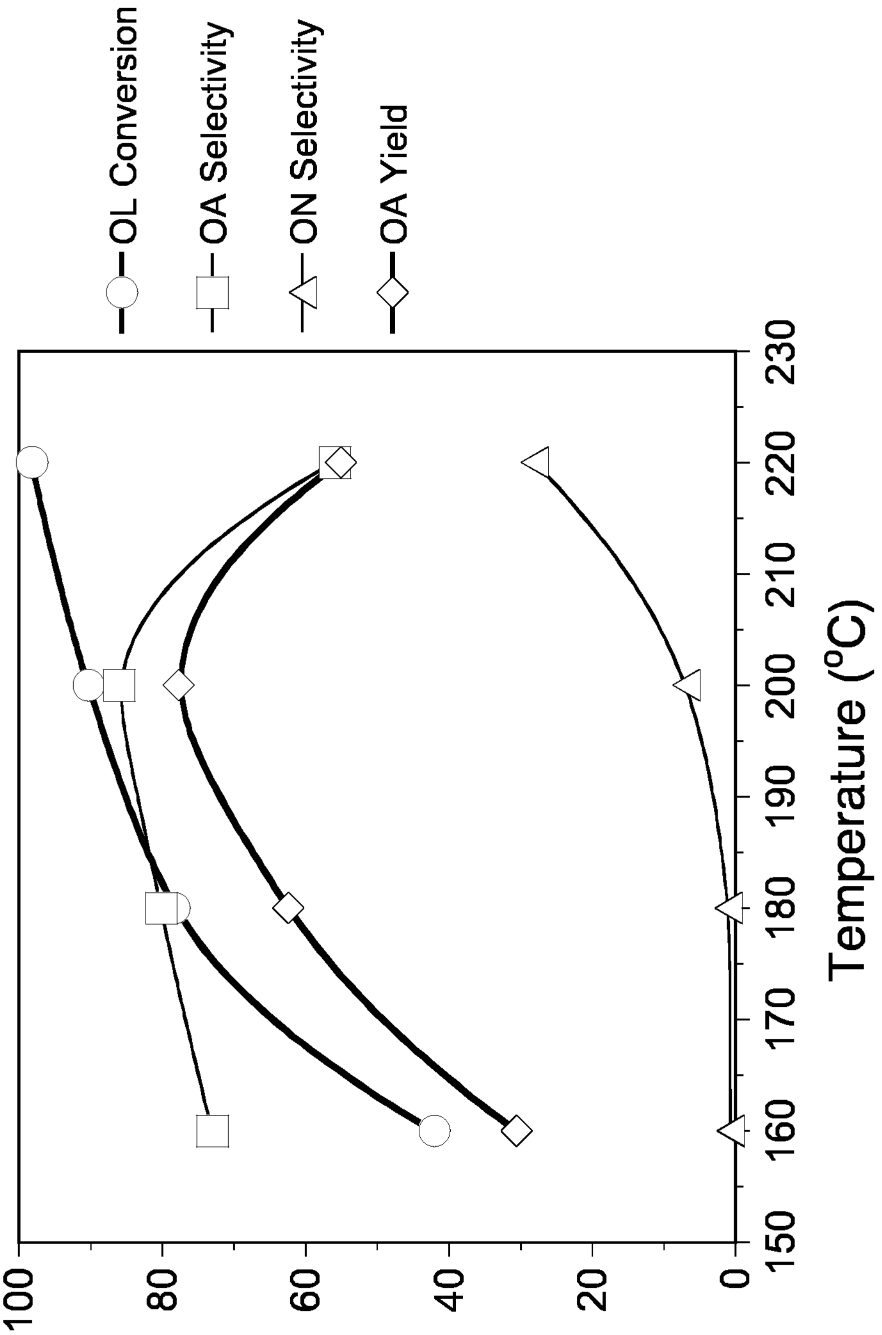

NH3 3 equiv. to OH
NH3 6 equiv. to OH
NH3 9 equiv. to OH
Yield OA (%)
0
5
10
15
20
25
30
35
40
0
5
10
15
20
12 kPa
PH2
60 kPa
H2 equiv. to OH
Co-Benchmark
Ag-Co
Co(Ru)

Figure 5


Conversion / Selectivity / Yield (%)
0
20
40
60
80
100
150
160
170
180
190
200
210
220
230
Temperature (°C)
OL Conversion
OA Selectivity
ON Selectivity
OA Yield

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/081274

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/02 B01J23/89 C07C209/14 C07C211/01
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 839 574 A2 (BASF AG [DE]) 6 May 1998 (1998-05-06) abstract page 4, lines 20-36 page 5, line 51 page 7, lines 29-38 example 4 -----	1-15
X	US 4 014 933 A (BASF AG) 29 March 1977 (1977-03-29) abstract column 2, lines 25-34 example 6 -----	1-15
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 8 July 2019	Date of mailing of the international search report 17/07/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fischbach, Malaika

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/093552 A1 (BASF AG [DE]; CAUWENBERGE GUNTHER VAN [BE] ET AL.) 23 August 2007 (2007-08-23) abstract page 5, lines 20-23 page 5, line 36 - page 6, line 2 page 6, lines 32-35 page 9, lines 32-35 example 1 -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/081274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0839574 A2	06-05-1998	CN 1181284 A	13-05-1998
		DE 19644107 A1	07-05-1998
		DE 59703662 D1	05-07-2001
		EP 0839574 A2	06-05-1998
		ES 2158423 T3	01-09-2001
		JP H10174874 A	30-06-1998
		US 5916838 A	29-06-1999
		US 6046359 A	04-04-2000
US 4014933 A	29-03-1977	NONE	
WO 2007093552 A1	23-08-2007	CN 101384541 A	11-03-2009
		EP 1986990 A1	05-11-2008
		JP 5124486 B2	23-01-2013
		JP 2009526810 A	23-07-2009
		US 2009030237 A1	29-01-2009
		WO 2007093552 A1	23-08-2007