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(54) Title: DIRECT AMINATION REACTION TO PRODUCE PRIMARY OR SECONDARY AMINE

(57) Abstract: A process for forming a primary or a secondary amine via a direct amination reaction is provided, which comprises reacting an alcohol with an amine in the presence of ordered porous manganese-based octahedral molecular sieves comprising a transition metal.



DIRECT AMINATION REACTION TO PRODUCE PRIMARY OR SECONDARY AMINE

The present invention concerns a process for forming a primary or a secondary amine via a direct amination reaction comprising: reacting an alcohol with an amine in the presence of ordered porous manganese-based octahedral molecular sieves comprising a transition metal.

PRIOR ART

Direct amination of alcohols is a very attractive pathway to prepare primary, secondary or tertiary amines. Various techniques have been described in the literature but usually require stringent conditions such as high temperature or high pressure of hydrogen. Also, such catalyst typically yields mixtures with average or low selectivity making purification difficult. Some attractive homogeneous catalysts have been developed recently and showed an improved selectivity relying on the "borrowing hydrogen" mechanism, which allows running the reaction under milder conditions and without the addition of hydrogen. However, homogeneous catalysts are expensive and difficult to recycle.

It is known from Zhang et al. Tetrahedron Letters 52 (2011) 1334–1338 the attractive properties of an iron oxide immobilized palladium catalyst for the N-alkylation of amines with alcohols. However this process leads also to tertiary amines in a significant amount.

Manganese octahedral molecular sieves (OMS) constitute a crystalline variety of amorphous manganese oxide (MnO_2) with a well-defined microporous network and different oxidation states of manganese. Among the different crystalline manganese oxide families (S.L. Suib, Accounts Chem. Res. 41 (2008) 479 ; Q.

Feng, H. Kanoh, K. Ooi, J. Mater. Chem. 41 (2008) 479), K-OMS-2 materials based on cryptomelane structure have proven excellent activities in the oxidation of alcohols (Y.C. Son, V.D. Makwana, A.R. Howell, S.L. Suib, Angew. Chem., Int. Ed. 9 (1999) 319.). Until now, the reported studies in K-OMS-2 materials point out the preferential generation of imines by N-alkylation of aromatic and aliphatic alcohols, but with no amine formation (S. Sithambaram, R. Kumar, Y-C. Son, S.L. Suib, J. Catal. 253 (2008) 269 ; S. Sithambaram, Y-C. Son, S.L. Suib, US Patent 7,355,075, 2008).

10 **INVENTION**

It appears now that a notable synergistic effect was identified by a combination of ordered porous manganese-based octahedral molecular sieves with transition metals in order to produce a primary or a secondary amine via a direct amination reaction of an alcohol with an amine. Such a catalyst may be used to produce a primary or a secondary amine with a very high selectivity and a very good conversion of amine without generating tertiary amine. The present catalytic system appears then to be very active for direct amination reaction of alcohols under mild conditions.

20 The present invention concerns then a process for forming a primary or a secondary amine via a direct amination reaction comprising reacting:

- A first reactant having one or two primary hydroxyl functionalities with
- A second reactant being NH_3 or a reactant having primary amine functionality,

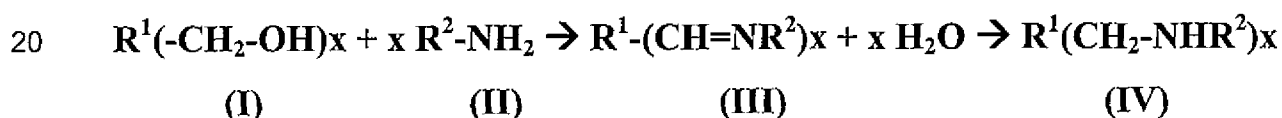
25 in the presence of ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table; and at a temperature and for a time sufficient for the primary amine or the secondary amine to be produced.

The present invention concerns furthermore this catalyst as such, i.e. ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table.

- 5 The present invention also concerns a primary or a secondary amine susceptible to be obtained by the process of the present invention.

The present invention also concerns a composition comprising at least an imine and a primary or a secondary amine, said composition is substantially free or, in
 10 some cases, completely free of tertiary amine. As used herein, the term "substantially free" when used with reference to the absence of tertiary amine in the composition of the present invention, means that the composition comprises less than 0.1 % wt of tertiary amine, based on the total weight of the composition. As used herein, the term "completely free" when used with
 15 reference to the absence of tertiary amine in the composition of the present invention, means that the composition comprises no tertiary amine at all.

Reaction of the present invention may notably be represented as follows:



Wherein:

- x is 1 or 2
- 25 - R¹ is H or a straight, branched or cyclic hydrocarbon group
- R² is H or a straight, branched or cyclic hydrocarbon group

While not being bound by theory, it is believed that the reaction of a first reactant having one or two primary hydroxyl functionalities with a second

reactant being NH_3 or a reactant having a primary amine functionality leads to the formation of an imine and a subsequent production of a primary or a secondary amine.

5 Definitions

“Alkyl” as used herein means a straight chain or branched saturated aliphatic hydrocarbon. Preferably alkyl group comprises 1-18 carbon atoms. Representative saturated straight chain alkyls include methyl, ethyl, n-propyl, n-butyl, n-pentyl, and the like; while saturated branched alkyls include isopropyl, sec-butyl, isobutyl, tert-
10 butyl, isopentyl, and the like.

“Alkenyl”, as used herein, refers to an aliphatic group containing at least one double bond and is intended to include both “unsubstituted alkenyls” and “substituted alkenyls”, the latter of which refers to alkenyl moieties having
15 substituents replacing a hydrogen on one or more carbon atoms of the alkenyl group. Representative unsaturated straight chain alkenyls include ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl and the like.

The term “cyclic group” means a closed ring hydrocarbon group that is
20 classified as an alicyclic group, aromatic group, or heterocyclic group. The term “alicyclic group” means a cyclic hydrocarbon group having properties resembling those of aliphatic groups.

“Aryl” as used herein means a 6-carbons monocyclic or 10-carbons bicyclic
25 aromatic ring system wherein 0, 1, 2, 3, or 4 atoms of each ring are substituted. Examples of aryl groups include phenyl, naphthyl and the like. The term “arylalkyl” or the term “aralkyl” refers to alkyl substituted with an aryl. The term “arylalkoxy” refers to an alkoxy substituted with aryl.

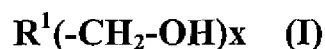
"Cycloalkyl" as used herein means cycloalkyl groups containing from 3 to 8 carbon atoms, such as for example cyclohexyl.

"Heterocyclic" as used herein means heterocyclic groups containing up to 6 carbon atoms together with 1 or 2 heteroatoms which are usually selected from O, N and S, such as for example radicals of : oxirane, oxirene, oxetane, oxete, oxetium, oxalane (tetrahydrofuran), oxole, furane, oxane, pyrane, dioxine, pyranium, oxepane, oxepine, oxocane, oxocinc groups, aziridine, azirine, azirene, azetidine, azetine, azete, azolidine, azoline, azole, azinane, tetrahydropyridine, tetrahydrotetrazine, dihydroazine, azine, azepane, azepine, azocane, dihydroazocine, azocinic groups and thiirane, thiirene, thiethane, thiirene, thietane, thiete, thietium, thiolane, thiole, thiophene, thiane, thiopyrane, thiine, thiinium, thiepane, thiepine, thiocane, thiocinic groups.

"Heterocyclic" may also mean a heterocyclic group fused with a benzene-ring wherein the fused rings contain carbon atoms together with 1 or 2 heteroatom's which are selected from N, O and S.

First reactant having one or two primary hydroxyl functionalities

This first reactant may notably be a compound of formula (I) :



Wherein:

- x is 1 or 2
- R^1 is H or a straight, branched or cyclic hydrocarbon group

R^1 may represent straight, branched or cyclic hydrocarbon group that can be an alkyl, alkenyl, aryl, cycloalkyl or heterocyclic group, eventually comprising one or several heteroatoms such as O, S, F, and N. Preferred groups for R^1 may be

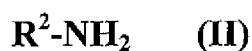
for example : H, alkyl, cyclic alkane, cyclic alkene, phenyl, furanyl, and tetrahydrofuranyl.

In addition the first reactant may comprise additional functionalities. The additional functionalities may behave as electron donating or electron withdrawing groups as long as their presence does not prevent reaction with the amine to form the imine. There is no particular limitation on the number of carbon atoms present in the reactant as long as its structure does not prevent the formation of the imine.

Preferred first reactants of the present invention, such as compounds of formula (I), are chosen in the group consisting of: furfuryl alcohol, 2,5 furandimethanol, 2,5-tetrahydrofuranedimethanol, benzyl alcohol, 1,6-hexandiol and 1,7-heptandiol.

Second reactant being NH_3 or a reactant having primary amine functionality

This second reactant may notably be a compound of formula (II) :



Wherein:

R^2 is H or a straight, branched or cyclic hydrocarbon group

R^2 may represent straight, branched or cyclic hydrocarbon group that can be an alkyl, alkenyl, aryl, cycloalkyl or heterocyclic group, eventually comprising one or several heteroatoms such as O, S, F, and N. Preferred groups for R^2 may be for example : H, alkyl, phenyl, benzyl, cycloalkyl, and cycloalkene.

In addition the second reactant may comprise additional functionalities. The additional functionalities may behave as electron donating or electron withdrawing groups as long as their presence does not prevent reaction with the amine to form the imine. There is no particular limitation on the number of carbon atoms present in the reactant as long as its structure does not prevent the formation of the imine.

Preferred second reactants of the present invention, such as compounds of formula (II), are chosen in the group consisting of: ammoniac, phenylamine, n-heptylamine, aniline and methylamine.

Imine

This imine produced by the reaction of first and second reactant may notably be a compound of formula (III) :



Wherein:

- x is 1 or 2
- R^1 is H or a straight, branched or cyclic hydrocarbon group
- R^2 is H or a straight, branched or cyclic hydrocarbon group

Preferred imines of the present invention, such as compounds of formula (III), are chosen in the group consisting of: N-phenylbenzylimine, (tetrahydrofuran-2,5-diyl)dimethanimine, (furan-2,5-diyl)dimethanimine, 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-methyliminomethane), 1,6-hexamethylenediimine, and 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-heptaneiminomethane).

Primary or secondary amine

The primary or secondary amine of the present invention may notably be a compound of formula (IV) :



Wherein:

- x is 1 or 2
- R^1 is H or a straight, branched or cyclic hydrocarbon group
- 10 - R^2 is H or a straight, branched or cyclic hydrocarbon group

Preferred primary or second amines of the invention, such as compounds of formula (IV), are chosen in the group consisting of : N-phenylbenzylamine, (tetrahydrofuran-2,5-diyl) dimethanamine, (furan-2,5-diyl) dimethanamine, 1,6-
 15 hexamethylenediamine, 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-methylmethylamine), and 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-heptaneaminomethane).

Reactions of the invention

20 Preferred reactions of the present invention are the following :

- Reaction of benzylalcohol (I) and aniline (II) to produce N-phenyl benzylimine (III) and N-phenyl benzylamine (IV)
- Reaction of 2,5-tetrahydrofurandimethanol (I) and ammonia (II) to produce (tetrahydrofuran-2,5-diyl)dimethanimine (III) and (tetrahydrofuran-2,5-
 25 diyl)dimethanamine (IV).
- Reaction of 2,5-furandimethanol (I) with ammoniac (II) to produce (furan-2,5-diyl)dimethanimine (III) and (furan-2,5-diyl)dimethanamine (IV).
- Reaction of 1,6-hexandiol (I) with ammoniac (II) to produce 1,6-hexamethylenediimine (III) and 1,6-hexamethylenediamine (IV)

- Reaction of 2,5-tetrahydrofuranedimethanol (I) with N-heptylamine (II) to produce 1,1'-(furan-2,5-diyl)bis(N-heptaneiminomethane) (III) and 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-heptaneaminomethane) (IV).

5 **Ordered porous manganese-based octahedral molecular sieves**

Ordered porous manganese-based octahedral molecular sieves (OMS) constitute an exemplary class of molecular sieves. These materials have one-dimensional tunnel structures and unlike zeolites, which have tetrahedrally coordinated species serving as the basic structural unit, these materials are based on six-
10 coordinate manganese surrounded by an octahedral array of anions (e.g., oxide).

Manganese oxide octahedral molecular sieves (OMS) possessing mono-directional tunnel structures constitute a family of molecular sieves wherein chains of MnO_6 octahedra share edges to form tunnel structures of varying sizes.
15 Such materials have been identified in samples of terrestrial origin and are also found in manganese nodules recovered from the ocean floor. Manganese nodules have been described as useful catalysts in the oxidation of carbon monoxide, methane and butane (U.S. Pat. No. 3,214,236), the reduction of nitric oxide with ammonia (Atmospheric Environment, Vol. 6, p.309 (1972)) and the
20 demetallation of topped crude in the presence of hydrogen (Ind. Eng. Chem. Proc. Dev.1, Vol. 13, p.315 (1974)).

The OMS framework topology is dictated by the type of arrangement of the MnO_6 octahedra, such as corner-sharing, edge-sharing, or face-sharing. The
25 ability of manganese to adopt multiple oxidation states and of the MnO_6 octahedra to adopt different arrangements affords the formation of a large variety of OMS materials. The OMS may further comprise an additional transition metal within the molecular framework as long as the incorporation of

the additional transition metal does not collapse the one-dimensional tunnel structure.

In one embodiment, the OMS catalyst comprises todorokites. Todorokites
5 include materials wherein the MnO_6 octahedra share edges to form triple chains and the triple chains share corners with adjacent triple chains to form a 3×3 tunnel structure. The size of an average dimension of these tunnels is about 6.9 Angstroms ($\text{\AA}$). A counter cation, for maintaining overall charge neutrality, such as Na, Ca, Mg, and the like is present in the tunnels and is coordinated to the
10 oxides of the triple chains. Todorokites are generally represented by the formula $(\text{M})\text{Mn}_3\text{O}_7$, wherein M represents the counter cation and manganese is present in at least one oxidation state. Further, the formula may also include waters of hydration and is generally represented by $(\text{M})_y\text{Mn}_3\text{O}_7 \cdot x\text{H}_2\text{O}$, where y is about 0.3 to about 0.5 and x is about 3 to about 4.5.

15 In one embodiment, the OMS catalyst comprises hollandites. Hollandites include a family of materials wherein the MnO_6 octahedra share edges to form double chains and the double chains share corners with adjacent double chains to form a 2×2 tunnel structure. The size of an average dimension of these tunnels
20 is about 4.6 $\text{\AA}$. A counter cation for maintaining overall charge neutrality such as Ba, K, Na, Pb, and the like, is present in the tunnels and is coordinated to the oxides of the double chains. The identity of the counter cation determines the mineral species or the structure type. Hollandites are generally represented by the formula $(\text{M})\text{Mn}_8\text{O}_{16}$, wherein M represents the counter cation and
25 manganese is present in at least one oxidation state. Further, the formula may also include waters of hydration and is generally represented by $(\text{M})_y\text{Mn}_8\text{O}_{16} \cdot x\text{H}_2\text{O}$, where y is about 0.8 to about 1.5 and x is about 3 to about 10. Suitable hollandites include hollandite ($\text{BaMn}_8\text{O}_{16}$), cryptomelane ($\text{KMn}_8\text{O}_{16}$), manjiroite ($\text{NaMn}_8\text{O}_{16}$), coronadite ($\text{PbMn}_8\text{O}_{16}$), and the like, and variants of at

least one of the foregoing hollandites. In one embodiment, the OMS catalyst comprises cryptomelane-type materials. In some embodiments some or all of the counter cation is H^+ .

- 5 In one embodiment, the OMS catalyst has an average Mn oxidation state of about 3 to about 4. Within this range the average oxidation state may be greater than or equal to about 3.2, or, more specifically, greater than or equal to 3.2, or even more specifically, greater than or equal to about 3.3. Average oxidation state may be determined by potentiometric titration.

10

In an exemplary method the OMS catalyst can be prepared by combining an aqueous solution of $KMnO_4$ (0.2 to 0.6 molar), an aqueous solution of $MnSO_4 \cdot H_2O$ (1.0 to 2.5 molar) and a concentrate acid such as HNO_3 . The aqueous solution is refluxed at $100^\circ C$ for 18-36 hours. The product is filtered,
15 washed and dried, typically at a temperature of 100 to $140^\circ C$. Similar procedures are known in the literature, for example, DeGuzman et al., Chem. Mater. 1994, 6, 815-821.

The OMS may be used in any form that is convenient, such as particulate,
20 aggregate, film or combination thereof. In addition, the OMS may be affixed to a substrate to facilitate separation of the catalyst from the product.

The hydrothermal method of synthesizing a manganese oxide octahedral molecular sieve possessing (2x2) tunnel structures similar to the naturally-
25 occurring hollandites is described in "Hydrothermal Synthesis of Manganese Oxides with Tunnel Structures," in Synthesis of Microporous Materials, Vol. II, 333, M. L. Occelli, H. E. Robson Eds. Van Nostrand Reinhold, N.Y., 1992. Such synthetic octahedral molecular sieves having (2x2) tunnel structures are referred to in the art by the designation OMS-2.

The hydrothermal method of producing OMS-2 involves autoclaving an aqueous solution of manganese cation and permanganate anion under acidic conditions, i.e., $\text{pH} < 3$, at temperatures ranging from about 80 to about 140°C in the presence of counter cations having ionic diameters of between about 2.3 and about 4.6 Å. The counter cations serve as templates for the formation of OMS-2 product and can be retained in the tunnel structures thereof. Based on analytical tests, OMS-2 produced via this method is thermally stable up to about 600°C.

Alternatively, OMS-2 can be produced by the method disclosed in R. Giovanili and B. Balmer, *Chimia*, 35 (1981) 53. Thus, when manganese cation and permanganate anion are reacted under basic conditions, i.e., $\text{pH} > 12$, a layered manganese oxide precursor is produced. This precursor is ion exchanged to form another layered manganese oxide which is then calcined at high temperatures, i.e., temperatures generally exceeding about 600°C, to form OMS-2 product. Analytical tests indicate that OMS-2 produced via this method is thermally stable up to about 800°C and the average oxidation state of manganese ion is lower.

The temperatures to produce OMS may be reached either thermically or via microwave irradiation.

Transition metal of Group 8 to 11 elements of the Periodic Table

A transition metal according to the present invention is a metal able to provide a reduction on imine, preferably on imine of formula (III), i.e. $\text{R}^1\text{-(CH=NR}^2\text{)}_x$

The transition metal is preferably chosen from the group consisting of Pd, Pt, Ru, Os, Ir, Ag, Au or a mixture thereof. More preferably the metal transition is a metal from the platinum group metals (PGMs), that are Pd, Pt, Rh, Ru, Ir and Os.

The preferable method to prepare ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table is the successive wet impregnation, or the co-precipitation, notably with the potassium permanganate and the magnesium sulfate under acidic conditions.

The activation or re-activation of the modified OMS catalysts may involve a calcination step and/or a reduction step under hydrogen. Notably, the activation of the modified OMS catalysts may involve a calcination step under air O₂ at 300-500°C for 1-24 hours and a reduction step under hydrogen at the same temperature for 1-6 hours according to M. Abecassis-Wolfovich et al. Applied Catalysis B: Environmental 2005, 59, 91).

The concentration of transition metal on the OMS carrier may be comprised between 0.1 and 20% by weight, preferably from 1 to 10% by weight.

The weight ratio of ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table to the second reactant may be comprised between 0.05 and 2, preferably from 0.1 to 0.5.

Conditions of the reaction

The reaction temperature may be comprised between 80 and 250°C. The reaction may be carried out in liquid or gas phase. In liquid phase, the reaction may be performed in the absence or presence of a solvent. The solvent is typically chosen based on its ability to dissolve the reactants.

The solvent may be protic, aprotic or a combination of protic and aprotic solvents. Exemplary solvents include toluene, octane, xylene, benzene, n-butanol, and acetonitrile. In some embodiments the solvent is a non-polar, aprotic solvent such as toluene. Solvents comprising hydroxyl functionalities or
5 amine functionalities may be used as long as the solvent does not participate in the reaction in place of the reactant.

The reactants, with an optional solvent, and the catalyst are typically combined in a reaction vessel and stirred to constitute the reaction mixture. The reaction
10 mixture is typically maintained at the desired reaction temperature under stirring for a time sufficient to form the primary or the secondary amine in the desired quantity and yield.

The reaction may be carried out in the presence of air but preferably with an
15 inert atmosphere such as N₂, Ar, CO₂ or even NH₃. Suitable oxygen containing gases include air, oxygen gas, and mixtures of oxygen gas with other gases such as nitrogen or argon. In some embodiments the oxygen containing gas is a flowing oxygen containing gas. In other embodiments the reaction vessel is charged with the oxygen containing gas.

20

The progress of the reaction toward the imine and the primary or secondary amine may be followed using an appropriate method such as thin layer chromatography, nuclear magnetic resonance, high-pressure liquid chromatography, gas chromatography or a combination of the foregoing
25 methods. Exemplary reaction times are 1 to 24 hours, preferably 1 to 8 hours.

The catalyst is typically removed from the reaction mixture using any solid/liquid separation technique such as filtration, centrifugation, and the like or

a combination of separation methods. The product may be isolated using standard isolation techniques, such as distillation.

In addition, the OMS catalyst can be reused. If desired, the catalyst can be regenerated by washing with methanol, water or a combination of water and methanol and subjecting the washed catalyst to a temperature of about 150°C to about 300°C for about 6 to 24 hours in the presence of oxygen.

The invention is further illustrated by the following non-limiting examples.

EXPERIMENTAL PART

Example 1: OMS Preparation

The preparation of the OMS catalyst used in the examples is as follows. 680 milliliters (ml) of potassium permanganate solution (40g) was added to a mixture of 173 ml manganese sulfate hydrate solution (54.4g) and 6.8 ml of concentrated nitric acid in a 1000 ml of round bottom flask with a condenser. The dark brown slurry was refluxed for 24 hours at 110°C, then filtered and washed with de-ionized water several times. The catalyst was dried at 120°C overnight before use. The composition of the K-OMS-2 catalyst was $\text{KMn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$ and the tunnels had dimensions of 4.6x4.6 angstroms. The average oxidation state of the manganese was approximately 3.8. The H-K-OMS-2 catalyst was generated by stirring the K-OMS-2 catalyst in a 1 Molar solution of nitric acid for 6 hours at 60-70°C for 6 hours.

The morphological and textural characteristics of the K-OMS-2 catalyst were inspected, respectively, by X-ray diffraction analysis and N_2 isotherm adsorption at 77.4 K. The XRD patterns for the fresh K-OMS-2 sample reveals the presence of a pure cryptomelane phase ($\text{KMn}_8\text{O}_{16}$, JCPDS 29, 1020). The K-OMS-2 catalyst show a high surface area ($143 \text{ m}^2/\text{g}$). The N_2 adsorption/desorption

isotherm plots for the K-OMS-2 catalyst reveal the presence of mesopores in the structure. The mesopore size range is between 17 and 62 nm, indicating a large amount of slit-shaped mesopores with uniform form sizes or shapes. Moreover, a sharp increase of the sorption loading is observed at low P/P_0 values, pointing
5 out the presence of micropores with a pore size of 0.36 nm.

The thermal stability of the K-OMS-2 material was studied by thermogravimetric analysis (TGA) under N_2 atmosphere in the range of 50-100°C with a ramp of 10°C/min. Four characteristic weight loss temperature ranges are
10 observed: (i) 50-200°C (1.2 %wt.), which is attributed to physisorbed O_2 and water; (ii) 350-550°C (3%), which is most likely attributed to chemisorbed oxygen and water; (iii) 550-700°C, involving the release of lattice oxygen from the manganese oxide; and (iv) 700-750°C, which is ascribed to the conversion of manganese Mn(IV) to lower oxidation states.

15

Example 2: Impregnation

The palladium/K-OMS-2 catalyst was prepared by dry impregnation of 1g of K-OMS-2. 7.03 mL of $Pd(NH_3)_4(NO_3)_2$ [Pd: 1.42 g/L] was added drop wise to the support. The mixture was stirred for 2 hours at 80°C. The slurry was dried in a
20 rota-evaporator first at 80°C for 2 hours and at 120°C overnight. Finally the solid was calcined at 350°C for 2 hours under oxygen.

Example 3: Synthesis of secondary amine / Proportion of catalysts

Benzylalcohol and aniline are used to produce the N-phenyl benzylimine (a) and
25 N-phenyl benzylamine (b) and eventually N-phenyl dibenzylamine (c).

Several proportions of catalysts were used with a molar ratio of aniline/benzyl alcohol = 1/3 in a sealed tube at a pressure of 1 bar, 160°C for 3 hours in an agitated medium (600 rpm) un N_2 .

After the reaction time the mixture was cooled and the catalyst was removed by filtration. The product mixture was analyzed by gas chromatography-FID [GC-FID]. The results are expressed in Table 1.

5

Table 1

Trials	Blank	K-OMS-2	Pd2%/K-OMS-2				
	1	2	3	4	5	6	7
Weight of Catalyst (mg)	0	60	7.5	15	30	60	90
Aniline conversion (%)	4	46	65	96	92	99	98
Selectivity a (%)	100	100	15	4	5	3	11
Selectivity b (%)	0	0	67	86	95	93	83
Selectivity c (%)	0	0	0	0	0	0	0

Another comparative trial was made by using 16 mg of Pd/Fe₂O₃ catalyst rather than the catalyst of the present invention, for 2h at 160 C, under N₂. It leads to a 100 % aniline conversion, 2% selectivity of imine, 94% selectivity of secondary amine and 4% selectivity of tertiary amine.

10

It appears then that the catalyst of the present invention permits to produce secondary amine with a very high selectivity and a very good conversion of aniline without generating tertiary amine.

15

Example 4: Synthesis of secondary amine / Time reaction

New trials were made according to Example 3 while using 60 mg Pd 2%/K-OMS-2 for 1, 3 or 6 hours. Results are expressed in Table 2

Table 2

Trials	1	2	3
Time (h)	1	3	6
Aniline conversion (%)	86	99	100
Selectivity a (%)	12	3	0
Selectivity b (%)	73	93	99
Selectivity c (%)	0	0	0

Example 5: Synthesis of secondary amine / Effect of the reaction atmosphere

- 5 New trials were made according to Example 3 while using 60 mg Pd 2%/K-OMS-2 for 3 hours under N₂ or O₂. Results are expressed in Table 3

Table 3

Trials	1	2
Reaction atmosphere	N ₂	O ₂
Aniline conversion (%)	99	98
Selectivity a (%)	3	36
Selectivity b (%)	93	56
Selectivity c(%)	0	0

- 10 It can be observed that a 100% aniline conversion is obtained under O₂ or N₂, but the selectivity of secondary amine is 93% under nitrogen atmosphere and decreases to 56% under O₂. These results are unexpected since OMS is considered as an oxidation catalyst and demonstrate the synergistic effect of the transition metal-OMS combination according to the present invention.

WHAT IS CLAIMED IS:

1. A process for forming a primary or a secondary amine via a direct amination reaction comprising reacting:

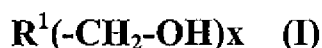
- 5 - A first reactant having one or two primary hydroxyl functionalities, with
 - A second reactant being NH_3 or a reactant having primary amine functionality,

in the presence of ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table;

- 10 and at a temperature and for a time sufficient for the primary amine or the secondary amine to be produced.

2. Process according to claim 1 wherein the first reactant is a compound of formula (I) :

15



Wherein:

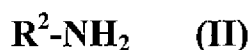
- x is 1 or 2
 - R^1 is H or a straight, branched or cyclic hydrocarbon group.

20

3. Process according to claim 2 wherein R^1 is an alkyl, alkenyl, aryl, cycloalkyl or heterocyclic group, eventually comprising one or several heteroatoms such as O, S, F, and N.

- 25 4. Process according to anyone of claims 1 to 3, wherein first reactants are chosen in the group consisting of: furfuryl alcohol, 2,5 furandimethanol, 2,5-tetrahydrofuranedimethanol, benzyl alcohol, 1,6-hexandiol and 1,7-heptandiol.

5. Process according to anyone of claims 1 to 4, wherein the second reactant is a compound of formula (II) :



5 Wherein:

R^2 is H or a straight, branched or cyclic hydrocarbon group.

6. Process according to claim 5 wherein R^2 is an alkyl, alkenyl, aryl, cycloalkyl or heterocyclic group, eventually comprising one or several heteroatoms such as
10 O, S, F, and N.

7. Process according to anyone of claims 1 to 6, wherein the second reactants are chosen in the group consisting of: ammoniac, phenylamine, n-heptylamine, aniline and methylamine.

15 8. Process according to anyone of claims 1 to 7, wherein the primary or second amine is a compound of formula (IV) :



20 Wherein:

- x is 1 or 2
- R^1 is H or a straight, branched or cyclic hydrocarbon group
- R^2 is H or a straight, branched or cyclic hydrocarbon group.

25 9. Process according to anyone of claims 1 to 8, wherein the primary or second amines are chosen in the group consisting of : N-phenylbenzylamine, (tetrahydrofuran-2,5-diyl) dimethanamine, (furan-2,5-diyl) dimethanamine, 1,6-hexamethylenediamine, 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-

methylethylamine), and 1,1'-(tetrahydrofuran-2,5-diyl)bis(N-heptaneaminomethane).

10. Process according to anyone of claims 1 to 9, wherein the ordered porous
5 manganese-based octahedral molecular sieves comprise todorkites.
11. Process according to anyone of claims 1 to 9, wherein the ordered porous manganese-based octahedral molecular sieves comprise hollandites.
- 10 12. Process according to anyone of claims 1 to 11, wherein the ordered porous manganese-based octahedral molecular sieves have an average manganese oxidation state of about 3 to about 4.
13. Process according to anyone of claims 1 to 11, wherein the transition metals
15 are chosen from the group consisting of : Pd, Pt, Ru, Os, Ir, Ag, Au or a mixture thereof.
14. Process according to anyone of claims 1 to 13, wherein the ordered porous manganese-based octahedral molecular sieves comprising a transition metal of
20 Group 8 to 11 elements of the Periodic Table are prepared by successive wet impregnation or co-precipitation.
15. Process according to anyone of claims 1 to 14, wherein the concentration of transition metal on the ordered porous manganese-based octahedral molecular
25 sieves is comprised between 0.1 and 20% by weight.
16. Process according to anyone of claims 1 to 15, wherein the weight ratio of ordered porous manganese-based octahedral molecular sieves comprising a

transition metal of Group 8 to 11 elements of the Periodic Table to the second reactant is comprised between 0.05 and 2.

17. Process according to anyone of claims 1 to 14, wherein the reaction
5 temperature is comprised between 80 and 250°C.

18. Process according to anyone of claims 1 to 17, wherein the reaction is carried out in liquid or gas phase.

10 19. Process according to anyone of claims 1 to 17, wherein the reaction is performed in the presence of a solvent.

20. Ordered porous manganese-based octahedral molecular sieves comprising a transition metal of Group 8 to 11 elements of the Periodic Table.

15

21. Composition comprising at least an imine and a primary or a secondary amine, said composition is substantially free or, in some cases, completely free of tertiary amine.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/082951

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: C07C209/-, C07C211/-, B01J23/-

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)

WPI, EPODOC, CNKI, CNPAT, MANGANESE, POROUS, OMS, OCTAHEDRAL, PALLADIUM, AMINE, ALCOHOL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YANG, Xiaojun et al. Effects of Pb dopant on structure and activity of Pd/K-OMS-2 catalysts for heterogeneous oxidative carbonylation of phenol, Catalysis Communications, January 2010, Vol. 11, pages 643-646, see page 644, Table 1.	20
A		1-19, 21
X	ZHANG, Yan et al. Palladium catalyzed N-alkylation of amines with alcohols, Tetrahedron Letters, January 2011, Vol. 52, pages 1334-1338, see page 1335 Table 1.	21
A		1-20
A	US 2007/0027344 A1 (THE UNIVERSITY OF CONNECTICUT) 01 February 2007 (01.02.2007), see claim 1.	1-21

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 14 June 2013(14.06.2013)	Date of mailing of the international search report 18 Jul. 2013 (18.07.2013)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer HAO, Peng Telephone No. (86-10)82246764

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/082951

Continuation of : CLASSIFICATION OF SUBJECT MATTER

C07C 209/14 (2006.01) i

C07C 209/00 (2006.01) i

C07C 211/00 (2006.01) i

B01J 23/34 (2006.01) i

B01J 23/00 (2006.01) i