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(54) Title: METAL SUPPORTED OXIDE NH3-SCR CATALYSTS HAVING HETERO-DUAL SITES AND SYNTHESIS PROCESSES

(57) Abstract: The present invention relates to processes for bimetallic grafting, on a support material which is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof, of (i) a combination of a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W), and a metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt, or (ii) a combination of tungsten (W) with vanadium (V) or niobium (Nb). The present invention further relates to catalyst materials as may be obtained by such processes, and to the use of such catalyst materials as an ammonia selective catalytic reduction (NH_3-SCR) catalyst for nitrogen oxides (NOx) reduction. The catalyst materials of the invention are of particular interest in providing improved NOx reduction performance in a low temperature range, notably 100°C to 250°C, particularly in the range of at least 130°C and at most 230°C.

METAL SUPPORTED OXIDE NH3-SCR CATALYSTS HAVING HETERO-DUAL SITES AND SYNTHESIS PROCESSES

Field of the Invention

[0001] The present invention relates to the synthesis of ammonia selective catalytic reduction (NH_3-SCR) catalysts for nitrogen oxides (NOx) reduction.

Background Art

[0002] Toxic NOx gases (NO, NO_2, N_2O) included in exhaust gases from fossil-fuel-powered vehicles or stationary sources such as power plants are required to be converted to N_2 before being released to the environment. This is normally done by using different types of NOx reduction catalysts such as three-way catalysts (TWC), NOx storage reduction (NSR), or selective catalytic reduction (SCR) using ammonia as external reducing agent (NH_3-SCR).

[0003] Metal oxides such as V_2O_5 are known to be good NH_3-SCR catalysts. It has been suggested that the catalytic activity is achieved by the complementary features of acidity and reducibility of the surface species. Briefly, NH_3 is adsorbed on a Brønsted acid site (V^{5+}-OH) followed by N-H activation through the adjacent V=O surface groups through a redox cycle (V^{5+}=O/V^{4+}-OH). The resulting surface complex reacts with gaseous or weakly adsorbed NO through Langmuir-Hinshelwood and Eley-Rideal mechanisms, respectively, to form NH_2NO intermediate species which undergo decomposition into N_2 and H_2O. An alternate mechanism (amide-nitrosamide) involving the adsorption of NH_3 over Lewis acid sites has also been proposed. Furthermore, under realistic conditions, particularly when a peroxidation catalytic convertor is placed upstream of the SCR catalytic convertor, this gives rise to formation of nitrogen dioxide which favors the SCR reaction known as fast-SCR. Indeed, NO_2 allows fast re-oxidation of the reduced species. However, the optimal NO_2/NO ratio is one, and the presence of excess NO_2 is also reduced through slower

reaction leading to a lower total SCR reaction rate. Metal oxide catalysts such as V_2O_5 are developed mostly by synthesis routes such as impregnation, which normally produce nanoparticles of metal dispersed on support. The problem of such catalysts is the low performance, such as low NOx conversion and/or low N_2 selectivity.

[0004] Prior art catalysts have often used Cu, Fe, which are well recognized as good active sites for NH_3-SCR when incorporated into zeolite materials. As regards support materials, prior art has often used SiO_2, which has high specific surface area, and may be expected to improve SCR performance by increasing the quantity of active sites.

US 9,283,548 B2 discloses catalysts of the type: MA / CeO_2 (M = Fe, Cu; A = K, Na), the synthesis route being impregnation, with chelating agents such as EDTA, DTPA being used.

J. Phys. Chem. B 2006, 110, 9593 – 9600 [Tian2006] discloses catalysts of the type: VOx / AO_2 (A = Ce, Si, Z), the synthesis route being impregnation. Applications include propane oxidative dehydrogenation (ODH). Dispersion and physisorption of the vanadium oxo-isopropoxide is achieved, rather than chemisorption.

J. Phys. Chem. B 1999, 103, 6015 – 6024 [Burcham1999] discloses catalysts of the type: Nb_2O_5 / SiO_2, Al_2O_3, ZrO_2, TiO_2, the synthesis route being impregnation. The reference discusses surface species of isolated Nb, characterized by vibrational spectroscopy. The preparation is carried out in water, and the metal is deposited on the surface, rather than being grafted by protonolysis.

J. Phys. Chem. C 2011, 115, 25368–25378 [Wu2011] discloses catalysts of the type:VOx / CeO_2, SiO_2, ZrO_2, the synthesis route being impregnation. Iso-propanol is used as a solvent, not leading to grafting of the precursor on the surface, but instead only dispersion and physisorption of the vanadium oxo-isopropoxide.

Appl. Catal. B 62, 2006, 369 [Chmielarz 2006] describes catalysts of the type: Fe or Cu/SiO_2 (3 different forms). It is widely known that Cu and Fe show good NH_3-SCR performance when zeolites are used (ion-exchange synthesis). The catalyst materials were used for deNOx by NH_3-SCR. Synthesis was carried out by molecular designed dispersion (MDD) using precursors $Fe(acac)_3$, Cu(acac)(acac = acetylacetonate).

Science 2007, 317, 1056-1060 [Avenier 2007] describes cleavage of dinitrogen on isolated silica surface-supported tantalum(III) and tantalum(V) hydride centers [$(\equiv Si\text{-}O)_2Ta^{III}\text{-}H$] and [$(\equiv Si\text{-}O)_2Ta^{V}\text{-}H_3$].

EP 2 985 077 A1 describes SiO_2-supported molybdenum or tungsten complexes, such as trialkyltungsten or molybdenum oxo complexes, their preparation and use in olefin metathesis.

[0005] The use of noble metals (platinum, Pt, palladium, Pd, rhodium, Rh) in catalytic convertors to promote the reactions and clean up the exhaust gas, has known for many years, largely used in a Three-Way-Catalyst (TWC). In addition to the metal components of modern TWCs, a complex mixture of precious-metal particles (Rh, Pt, Pd) and various oxide materials are included in the catalyst's formulation. Rhodium is included in the formulation of TWC for its superior capacity to catalyse the reduction of NO in reducing atmosphere-containing unused hydrocarbons. The usual precursor of rhodium is $Rh_4(CO)_{12}$ with a structure described as a tetrahedral array of four Rh atoms with nine terminal CO ligands and three bridging CO ligands. Isolated species of $Rh(CO)_2$ have been obtained from zerovalent [$Rh_4(CO)_{12}$] cluster precursors on alumina (*Chem. Rev.* 2002, 102, 9, 3085–3128).

Summary of the Invention

[0006] In order to address the problems associated with prior art products and processes in the field of ammonia selective catalytic reduction (NH_3-SCR) catalysts for nitrogen oxides (NOx) reduction, the processes and

products of the present invention have been developed. Combinations of transition metal loading of ceria and zirconia oxides have been optimized in terms of catalytic performance. In particular, among catalyst materials of the present invention are ones showing improved low temperature performance. Indeed, in the field of exhaust gas catalysis in conventional fuel-powered cars, the so-called cold-start period (immediately after the engine starts) is known to be a problem for catalytic performance. During this period, the temperature ranges from room temperature to about 250°C, where catalytic reactions are more generally activated. In cars with a hybrid chassis, i.e. partially powered by an electric engine, the average temperature of exhaust gas is even lower, making the issue of low-temperature catalyst performance more critical. It is therefore of particular interest to provide new catalysts with improved NOx reduction performance in a low temperature range, such as 100°C to 250°C, to address this issue.

[0007] The Surface Organometallic Chemistry (SOMC) approach is capable of modifying the surface of support materials by grafting organometallic precursors, i.e. forming chemical bonds between precursors and surface hydroxyl groups, and thus preserving the local structure of the grafted material to minimize the formation of diversified species on the surface of support materials that are normally created through conventional synthesis methods. This methodology can be used to synthesize metal oxide catalysts supported with different metals. A typical SOMC procedure to synthesize materials consists of 3 steps as follows:

- Step 1: Preparation, example:
    - Support materials:
        - calcination
        - hydration
        - dehydroxylation to generate controlled concentrations of hydroxyl groups

- Metal precursors:
  - Synthesis (for those that are not readily available)
- Step 2: Grafting
  - Allow metal precursors to react with surface hydroxyl groups of the support material in a solution, for example toluene, typically at room temperature (~ 25 °C)
  - Washing and drying
- Step 3: Activation
  - Remove remaining organic ligands, typically by calcination at around 500 °C or higher in 16 h under air flow

[0008] The present invention discloses the development of new oxide NH_3-SCR catalysts with improved NOx reduction performance by using new SOMC procedures.

[0009] Thus, in a first embodiment of a first aspect, the present invention relates to a process for preparing a catalyst material, comprising the steps of:

(a) providing a support material having surface hydroxyl (OH) groups, wherein the support material is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof;

(b) reacting the support material having surface hydroxyl (OH) groups of step (a) with a first precursor compound containing a metal element;

(c) heating the material obtained in step (b), having a grafted metal element, in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

(d) regenerating surface hydroxyl (OH) groups on the material obtained in step (c);

(e) reacting the support material having surface hydroxyl (OH) groups of step (d) with a second precursor compound containing a metal element different to the metal element of the first precursor compound;

(f) heating the material obtained in step (e), having grafted metal elements from both the first and second precursor compounds, in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour, so as to prepare a catalyst material,

wherein one of the first and second precursor compounds is a compound (L) containing a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W), and the other precursor compound is a compound (R) containing a metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt.

[0010] In a second embodiment of the first aspect, the present invention relates to a process for preparing a catalyst material, comprising the steps of:

(a) providing a support material having surface hydroxyl (OH) groups, wherein the support material is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof;

(b) reacting the support material having surface hydroxyl (OH) groups of step (a) with a first precursor compound containing a metal element;

(c) heating the material obtained in step (b) having a grafted metal element in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

(d) regenerating surface hydroxyl (OH) groups on the heated material containing a grafted metal element obtained in step (c);

(e) reacting the support material having surface hydroxyl (OH) groups of step (d) with a second precursor compound;

(f) heating the material obtained in step (e) in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

wherein one of the first or second precursor compounds contains tungsten (W) and the other precursor compound contains vanadium (V) or niobium (Nb), and wherein the calcined catalyst material obtained by step (f) has at least 0.6 wt% and at most 1.4 wt% of tungsten (W), and either at least

0.8 wt% and at most 1.6 wt% of niobium (Nb) or at least 0.5 wt% and at most 1.1 wt% of vanadium (V).

[0011] Preferably, in the second embodiment of the first aspect, the calcined catalyst material obtained by step (f) has at least 0.8 wt% and at most 1.2 wt% of tungsten (W), and either at least 1.0 wt% and at most 1.4 wt% of niobium (Nb) or at least 0.6 wt% and at most 1.0 wt% of vanadium (V). More preferably, the calcined catalyst material obtained by step (f) has at least 0.9 wt% and at most 1.1 wt% of tungsten (W), and either at least 1.1 wt% and at most 1.3 wt% of niobium (Nb) or at least 0.7 wt% and at most 0.9 wt% of vanadium (V).

[0012] The embodiments of the first aspect of the present invention thus provide processes for bimetallic grafting, on a support material which is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof, of (i) a combination of a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W), and a metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt, or (ii) a combination of tungsten (W) with vanadium (V) or niobium (Nb).

[0013] In a second aspect, the present invention relates to a catalyst material as may be obtained by the processes set out above.

[0014] In a third aspect, the present invention relates to the use of the catalyst material set out above as an ammonia selective catalytic reduction (NH_3-SCR) catalyst for nitrogen oxides (NOx) reduction. As mentioned above, the catalyst materials of the invention are of particular interest in providing improved NOx reduction performance in a low temperature range, notably 100°C to 250°C, particularly in the range of at least 130°C and at most 230°C.

Brief description of the Figures

[0015] Figures 1 to 3 show NH_3-SCR NOx reduction of catalysts synthesized by SOMC (Surface Organometallic Chemistry) processes, and specifically the performance of illustrative Nb-based hetero-dual site catalysts in

comparison to an Nb-only catalyst, all on a ceria (CeO_2) support. The numbers (1.2 etc.) after metal elements in the legends identifying the catalysts giving rise to the different plotted curves indicate metal loading as a weight percentage.

Figures 4 to 6 show NH_3-SCR NOx reduction of catalysts synthesized by SOMC (Surface Organometallic Chemistry) processes, and specifically the performance of illustrative hetero-dual site catalysts in comparison to an Nb-only catalyst, all on a ceria (CeO_2) support. Figures 4 to 6 show, respectively, the performance of illustrative Nb-Rh, V-Rh and W-Rh hetero-dual site catalysts.

Figure 7 shows DRIFT spectroscopy analysis spectra of a) ceria dehydroxylated at 200 °C ($CeO_{2\text{-}200}$) and b) after grafting of $Rh_4(CO)_{12}$.

Figure 8 shows DRIFT spectra of a) grafting of $Rh_4(CO)_{12}$ on ceria dehydroxylated at 200 °C, b) after thermal treatment at 250 °C under vacuum (10^{-5} Torr) and c) after calcination of the later at 400°C under dry air.

Figure 9 shows physisorption isotherms of nitrogen at 77 K of the material containing 1 wt% of Rh on ceria after calcination under dry air at 400 °C for 16 h.

Figure 10 shows DRIFT spectra of a) RhO_x-$CeO_{2\text{-}200}$ material dehydroxylated at 200 °C, b) grafting of $W(\equiv C^tBu)(CH_2{}^tBu)_3$ on RhO_x-$CeO_{2\text{-}200}$, c) preparation of bimetallic Rh-W catalyst through calcination at 500 °C for 16h under dry air.

Figure 11 shows physisorption isotherms of nitrogen at 77 K of the material containing 1 wt% of Rh and 0.98 wt% of W on ceria.

Detailed description of the invention

[0016] In the present invention, a process of grafting (chemical reactions between precursors and surface) is used rather than impregnating. A support material selected from CeO_2, ZrO_2 or their mixtures such as CeO_2-ZrO_2

is used and is treated in such a way as to generate desired anchoring points (OH groups).

[0017] The catalysts prepared in the first embodiment of the first aspect of the present invention comprise both (1) at least one metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W); and (2) at least one metal element selected from the group consisting of: Ru, Fe, Mn, Rh, Ir, Pd and Pt.

[0018] In practice, the metal elements of types (1) and (2) are grafted in successive steps, with a fresh generation of OH-bearing support material between each grafting step.

[0019] Figures 1, 2 and 3 show NOx transformation performance of catalysts containing two metals. After grafting with a Group 5 or Group 6 metal, in particular Nb, V or W, a second grafting is carried out using either a further Group 5 or Group 6 metal, or a separate transition metal. It appears that a separate loading of a further Group 5 or Group 6 metal may provide improved catalyst performance in certain temperature ranges, in a synergistic effect. Conversely, addition of Cu decreases activity compared to single metal catalysts i.e. ones only loaded with a Group 5 or Group 6 metal.

[0020] Of particular interest in the present invention is an improvement in low-temperature catalyst performance, which was not observed to be obtainable through mixtures of Group 5 and 6 metals, or mixtures of Group 5 and 6 metals with Cu. It was observed that catalysts containing 1.0 wt% of W and 0.8 wt of V show higher NOx reduction than reference catalysts in the range 150 to 200°C, but in fact show improvements over a much broader temperature range. Without wishing to be bound by any particular theory, it is postulated that the effect observed may result from an increase in the number of active sites rather than a special effect such as a change in chemical mechanism.

[0021] In the framework of the present invention, comparisons of catalytic performance were made between samples with only Nb metal loaded

on the support (1.8 wt%, or 3.4 wt% by grafting two times), Rh (1 wt%) alone, and Nb in combination with Rh. Improved NOx reduction in the (low) temperature range of 130 to 230°C was investigated. The use of a high Nb loading shows improved performance at high temperature but actually reduced performance at low temperature (compared to a lower loading of Nb alone). Similar effects were observed experimentally with V or W instead of Nb as Group 5/6 metal. The combination of both a Group 5/6 metal atom and a metal element such as Rh therefore appears to create a special synergistic effect as regards low temperature catalytic performance.

[0022] Appropriate support materials in the form of ceria (CeO_2) and/or zirconia (ZrO_2) can be obtained from commercial suppliers. For example, ceria can be obtained from suppliers such as SOLVAY and typically has a specific surface area of about 250 m^2/g.

[0023] In an advantageous embodiment to provide a certain controlled concentration of OH groups on the support material, in order to provide the material in step (a) of the process of the invention, hydration of the oxide support material (as received in a typical commercial sample) may be carried out in a first instance using moisture, followed by dehydroxylation through heating under reduced pressure. For this step the solid support material may appropriately be put in close contact with a vapour pressure of water for ca. 10 min., a sufficient duration to allow a physical and chemical adsorption of water. The vapour pressure of water at 25°C is 16 Torr. In a generally appropriate way to proceed, one may allow sufficient time for the adsorption of an excess of water from a glass reactor on the surface of the support.

[0024] The concentration of OH groups is notably influenced by the temperature of the treatment. In a generally appropriate process for treating a ceria (CeO_2) support material, a pressure of about 10^{-5} mbar, at a temperature of 200 °C for typically 16 h, constitute advantageous treatment conditions. Generally appropriate temperature ranges are from 150 °C to 550 °C,

preferably from 200°C to 350°C, with a treatment time 4 h to 24 h preferably from 10 h to 16 h, with pressures 10^{-3} mbar to 10^{-6} mbar. The concentration of OH groups on the support material can for example be determined by chemical titration through reaction with $Al(^{i}Bu)_3$ - the latter reacts quantitatively with surface hydroxyl groups releasing one equivalent of isobutane per OH group.

[0025] In regeneration step (d), for the regeneration of appropriate ranges of OH groups on the support after the heating in step (c) to fix a first metal element, the conditions in terms of quantity of water added, temperature and pressure and duration, for adding moisture and heating under low pressure to dehydroxylate / produce a controlled quantity of OH groups, are generally the same as in step (a), and process conditions in final heating step (f) are generally the same as in heating step (c). Thus, in the processes according to the invention, the support material provided in step (a), and/or the support material obtained by regeneration in step (d), contain(s) at least 0.3 mmol and at most 2.0 mmol OH groups/g of the support material, and preferably at least 0.5 mmol and at most 1.3 mmol OH groups/g of the support material.

[0026] Preferred support materials in the present invention are ceria (CeO_2) or ceria-zirconia (CeO_2 – ZrO_2) supports. Concerning the mixed ceria-zirconia (CeO_2 – ZrO_2) support, the amount of ZrO_2 can be in the range 20-80 wt%, preferably between 30-60 wt%. A higher content of ZrO_2 may in practice decrease the concentration of OH groups. CeO_2 and CeO_2-ZrO_2 are not known in the prior art as good support materials for SCR catalysts - these materials normally have lower specific surface area (SSA) than SiO_2.

[0027] Concerning the functionalization (grafting) stages, constituted by steps (b) and (e) of the processes of the first or second embodiment of the first aspect of the present invention, generally appropriate solvents include apolar solvents, such as in particular hydrocarbon solvents. Specific example of solvents include: pentane, hexane, heptane, toluene, xylenes, and mesitylene. In terms of reaction conditions for grating, temperatures may range from room

temperature up to reflux conditions and the reaction time may appropriately be from 1 hour to 60 hours.

[0028] Concerning the activation (calcination) stages, constituted by steps (c) and (f) of the processes of the first or second embodiment of the first aspect of the present invention, the activation process may be carried out at temperatures from 400 °C – 700 °C, preferably between 300 °C and 600 °C. Calcination may appropriately be carried out in an oxygen-containing atmosphere, such as dry air.

[0029] In preferred processes according to the first embodiment of the first aspect of the present invention, the compound (L) is:

(A) a compound containing at least one alkoxy or phenoxy group bound though its oxygen atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W); or

(B) a compound containing at least one hydrocarbon group bound though a carbon atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W).

[0030] In preferred embodiments, compound (A) containing at least one alkoxy or phenoxy group bound though its oxygen atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W) is at least one compound selected from the group consisting of: $[Nb(OEt)_5]_2$; $Nb(OAr)_5$ where Ar is the 1,3,5-trimethylphenyl $(CH_3)_3C_6H_2$- group; $[W{=}O(OEt)_4]_2$; $[W(O)(O^tBu)_4]$; $[W_2(O^tBu)_6]$; $[V(=O)(OEt)_3]_2$; $[V(=O)(O^iPr)_3]$; and $[Ta(OEt)_5]_2$.

[0031] In preferred embodiments, compound (B) containing at least one hydrocarbon group bound though a carbon atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W) is at least one compound selected from the group consisting of: $W(=NR)(=CH^tBu)_2(CH_2{}^tBu)_2$ (R = alkyl or aryl); $W(=O)(CH_2{}^tBu)_3Cl$; $W(\equiv C^tBu)(CH_2{}^tBu)_3$; $[(^tBuCH_2)_3W]O$; $[(^tBuCH_2)_3W{=}O]_2(\mu\text{-}O)$; $[^tBuO_3W{=}O]_2(\mu\text{-}O)$; $(^tBuO)_3W{\equiv}W(^tBuO)_3$;

$Mo(=O)(CH_2{}^tBu)_3Cl$; $Mo(O)_2Mesityl_2$; $V(=O)Mes_3$; $V(=O)CH_2SiMe_3$; $Ta(=CH^tBu)(CH_2{}^tBu)_3$.

[0032] In preferred embodiments, compound (R) is a compound having alkyl, aryl, alkenyl and/or carbonyl groups bound to the metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt. Preferably, the compound (R) is selected from the group consisting of: $Rh(\eta^3\text{-allyl})_3$; $Rh_4(CO)_{12}$; $Fe(Mesityl)_2$; $Fe(CO)_5$; $Mn(CH_2{}^tBu)_2$; $Me_5CpPtMe_4$; $Pd(dba)_2$; $Pd(COD)(CH_2SiMe_3)_2$; CpPdMe; $Pt(COD)Me_2$.

[0033] In particularly preferred embodiments of processes according to the first embodiment of the first aspect of the present invention, the compound (R) contains rhodium (Rh) or iron (Fe), and/or the compound (L) contains one or more of: tungsten (W), niobium (Nb) and vanadium (V), most preferably tungsten (W).

[0034] In particularly preferred embodiments of processes according to the first embodiment of the first aspect of the present invention, the calcined catalyst material obtained by step (f) has at least 0.5 wt% and at most 9.0 wt%, preferably at least 1.0 wt% and at most 6.0 wt%, of metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W). More preferably, the calcined catalyst material obtained by step (f) has at least 0.5 wt% and at most 6.0 wt%, preferably at least 1.0 wt% and at most 6.0 wt%, of metal element selected from the group consisting of: Ru, Mn, Fe, Rh, Ir, Pd and Pt.

[0035] In preferred processes according to the second embodiment of the first aspect of the present invention, the first and second precursor compounds are:

(A) a compound containing at least one alkoxy or phenoxy group bound though its oxygen atom to V, Nb or W; or

(B) a compound containing at least one hydrocarbon group bound though a carbon atom to V, Nb or W.

[0036] In particularly preferred processes according to the second embodiment of the first aspect of the present invention, compound (A) containing at least one alkoxy or phenoxy group bound though its oxygen atom to V, Nb or W is at least one compound selected from the group consisting of: $[Nb(OEt)_5]_2$; $Nb(OAr)_5$ where Ar is the 1,3,5-trimethylphenyl $(CH_3)_3C_6H_2$- group; $[W{=}O(OEt)_4]_2$; $[W(O)(O^tBu)_4]$; $[W_2(O^tBu)_6]$; $[V(=O)(OEt)_3]_2$; and $[V(=O)(O^iPr)_3]$. In particularly preferred processes according to the second embodiment of the first aspect of the present invention, compound (B) containing at least one hydrocarbon group bound though a carbon atom to V, Nb or W is at least one compound selected from the group consisting of: $W(=NR)(=CH^tBu)_2(CH_2{}^tBu)_2$ (R = alkyl or aryl); $W(=O)(CH_2{}^tBu)_3Cl$; $W(\equiv C^tBu)(CH_2{}^tBu)_3$; $[(^tBuCH_2)_3W]O$; $[(^tBuCH_2)_3W{=}O]_2(\mu\text{-}O)$; $[^tBuO_3W{=}O]_2(\mu\text{-}O)$; $(^tBuO)_3W{\equiv}W(^tBuO)_3$; $V(=O)Mes_3$; $V(=O)CH_2SiMe_3$.

[0037] Catalyst materials prepared in the present invention may be used as NH_3-SCR catalysts. Hydrocarbons may also be envisaged as reductant instead of ammonia for NOx reduction.

[0038] Catalyst materials of the present invention can interact with gas reactants in a catalytic process. In certain embodiments the catalyst materials may be applied to an inert substrate such as a metal plate, corrugated metal plate, or honeycomb. Alternatively, the catalyst material may be combined with other solids such as fillers and binders in order to provide an extrudable paste that may be transformed into a porous structure such as a honeycomb.

[0039] A catalytic converter based on catalyst materials of the present invention may appropriately include the catalyst material disposed on a supporting element such that passages are made available for the passage of exhaust gases, and the supported catalyst material may appropriately be housed in a metal casing. The metal casing is generally connected with one or more inlets such as pipes for transferring exhaust gases towards the catalyst material.

[0040] In order to function in NH_3-SCR catalysis, the catalytic converter is appropriately connected with a source of ammonia in order for the latter to come into contact with exhaust gas. The ammonia can be provided as anhydrous ammonia, aqueous ammonia, urea, ammonium carbonate, ammonium formate, or ammonium carbamate. In some embodiments, an ammonia storage tank is used to contain the ammonia source.

[0041] An SCR system can be integrated into various systems that require NOx reduction. Applications include engine systems of a passenger vehicle, truck, utility boiler, industrial boiler, solid waste boiler, ship, locomotive, tunnel boring machine, submarine, construction equipment, gas turbine, power plant, airplane, lawnmower, or chainsaw. Catalytic reduction of NOx using catalyst materials according to the present invention is therefore of general interest in situations where fossil fuels are used for power generation, not just for transportation but also in power generation devices, and domestic appliances using fossil fuels. Catalysts according to the present invention may be notably used in vehicles partially powered by electric engines.

[0042] Within the practice of the present invention, it may be envisaged to combine any features or embodiments which have hereinabove been separately set out and indicated to be advantageous, preferable, appropriate or otherwise generally applicable in the practice of the invention. The present description should be considered to include all such combinations of features or embodiments described herein unless such combinations are said herein to be mutually exclusive or are clearly understood in context to be mutually exclusive.

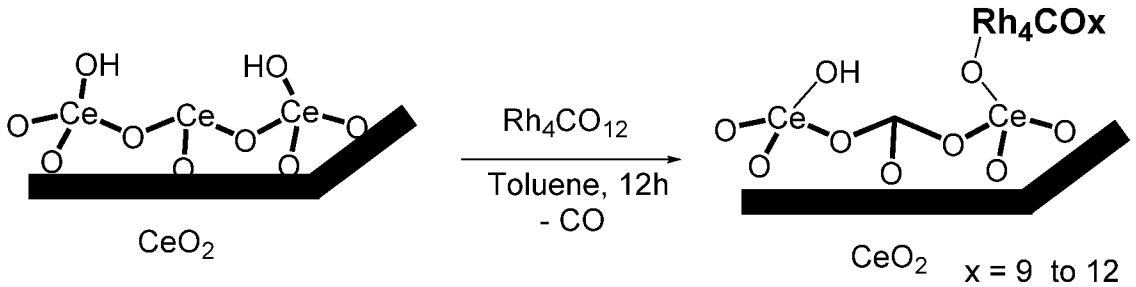
Experimental section – Examples

[0043] The following experimental section illustrates experimentally the practice of the present invention, but the scope of the invention is not to be considered to be limited to the specific examples that follow.

Part A: Preparation of bimetallic RhOx/MOx/CeO_2 catalysts through SOMC approach (M = W, V, Nb)

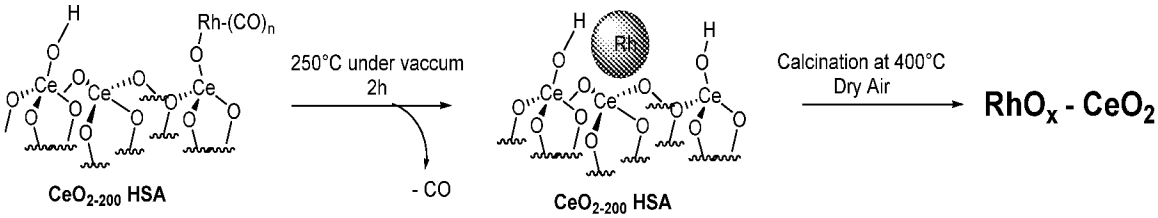
Preparation Example A1: First step - Preparation of RhOx/CeO_2 through SOMC approach

[0044] A mixture $CeO_{2(200)}$ (6 g) and a desired amount of tetrarhodium dodecacarbonyl as a dark-red crystalline solid (109 mg to reach *ca.* 1 wt% of Rh) was stirred at 25 °C in toluene (20 ml) for 12 h. After filtration, the solid $[Rh_4(CO)_{12}]$-$CeO_{2-(200)}$ was heated at 60 °C under vacuum (10^{-5} mbar) in order to remove the unused complex and to promote the formation of isolated Rh/CeO_2 species. In a second variant, this catalyst was prepared via CVD $[Rh_4(CO)_{12}]$ (a solid/solid phase reaction - Scheme 1). Thus a mixture of $[Rh_4(CO)_{12}]$ (37 mg, 0.05 mmol) and CeO_{2-200} (1 g) was stirred at 25 °C for 12 h. Then the unreacted $Rh_4(CO)_{12}$ was removed through sublimation at 60 °C under vacuum (10^{-5} Torr).



Scheme 1 : Surface organometallic reaction of $Rh_4(CO)_{12}$ with surface hydroxides of CeO_2 dehydroxylated at 200 °C

[0045] The grafting reaction of $Rh_4(CO)_{12}$ on ceria to form $[Rh_4(CO)_{12}]$-$CeO_{2-(200)}$ is monitored by DRIFT spectroscopy (Figure 7). After the grafting reaction and the removal of the excess complex, the bands between 3400 and 3700 cm^{-1} attributed to different vibration mode of v(CeO-H) were disturbed. The band at 3747 cm^{-1} completely disappeared, and others were shifted. New bands in the 2100-1900 cm^{-1} range were observed - these peaks are characteristic of CO stretching vibrations of the chemisorbed ligands on the surface. Peaks at 2082 and 2008 cm^{-1} are attributable to symmetric and to asymmetric geminal dicarbonyl species $[Rh-(CO)_2]$ respectively. The signal at 2059 cm^{-1} can be assigned to linear CO species and the band at 1918 cm^{-1} is presumably due to the bridged CO species.



Scheme 2: Schematic representation of surface organometallic species $Rh_4(CO)_{12}$]-$CeO_{2-(200)}$ (a) °C evolution with the different treatments by pyrolysis under vacuum at 250°C (b) and calcination at 400°C under dry synthetic air

[0046] Pyrolysis of $[Rh_4(CO)_{12}]$-$CeO_{2-(200)}$ material at 250 °C under vacuum resulted in the removal of the carbonyl ligands as confirmed by disappearance of the bands in the region between 1900 and 2100 cm^{-1} in DRIFT spectrum shown in Figure 8-b, characteristic of v(CO) vibrations. The brown sample becomes black suggesting the formation of Rh nanoparticles on the ceria support.

[0047] After calcination at 400 °C under dry air (15 h) (Figure 8 c), bands between 3400 and 3700 cm^{-1} attributed to different vibration mode of v(CeO-H) are observed - this portion of hydroxyl groups can be further functionalized by other organometallic to yield heterobimetallic catalyst on CeO_2 support.

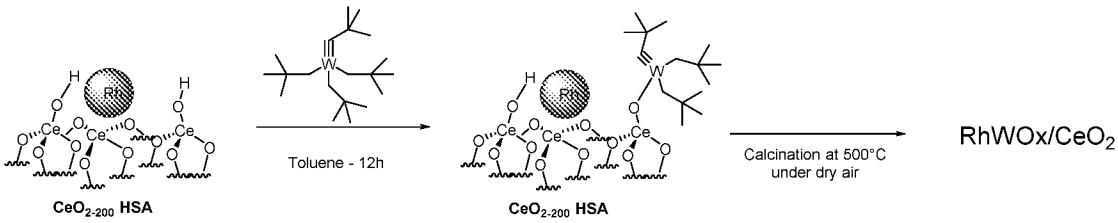
[0048] The BET surface area measured for the resulting material was found to be ca. 176 ± 9 m^2/g, close to the one found for the neat ceria calcined under the same conditions, which was ca. 200 ± 10 m^2/g. This would mean that the crystal structure of ceria support is preserved and the grafting as well as the calcination process induce no particle sintering.

[0049] In addition to creating an additional anchoring site, the material $\{RhO_x\}$-CeO_2 obtained in the first step (Schemes 1 and 2) was rehydrated by addition of vapor pressure of water. The sample was heated at 100 °C for 6 h in the presence of the moisture. Afterwards, the material was dehydroxylated under high vacuum (10^{-5} Torr) at 200 °C, and the excess as well as the physisorbed water were removed.

Example A2-a: Grafting of [W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$]-on RhOx-CeO$_2$ through SOMC approach : (WOx-RhOx/CeO$_2$) (Rh 1.0; W 2.5)

[0050] A mixture of W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$ (193 mg) and RhO_x-$CeO_{2\text{-}200}$ (2 g) was stirred in toluene for 4 h, at room temperature. The W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$/RhO_x-$CeO_{2\text{-}200}$ material was washed three times with pentane via filtration-condensation cycles. Then, all volatiles were condensed into a 6 L vessel in order to quantify neopentane evolved during the grafting reaction. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0051] The grafting reaction (Scheme 3) was monitored by DRIFT spectroscopy.



Scheme 3: Surface organometallic reaction of $W(\equiv C^tBu)(CH_2{}^tBu)_3$ on RhO_x-$CeO_{2\text{-}200}$ and preparation of bimetallic Rh-W catalyst through subsequent calcination

[0052] As shown in Figure 10, after surface functionalization of the ceria surface by $W(\equiv C^tBu)(CH_2{}^tBu)_3$, the bands between 3500 and 3700 cm^{-1} attributed to different vibration modes of surface ν(O-H) are disturbed. Indeed, the DRIFT spectrum of the resulting material (Figure 10 b) shows a partial consumption of the other OH vibration bands, located between 3700 and 3600 cm^{-1}, while a new broad band appears, resulting from the interaction of some OH groups with tungsten alkyl ligands. The new bands appearing in the 3100-2850 cm^{-1} and 1620-1400 cm^{-1} ranges are characteristic of aliphatic ν(C−H), and δ(C−H) vibrations of the perhydrocarbyl ligands coordinated to surface tungsten.

[0053] The material of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$-$RhO_x$-$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to catalyst (Rh 1.0, W 2.5). The recovered material prior to catalytic test was characterized. The DRIFT analyses showed the complete disappearance of CH group of the perhydrocarbyl moieties and the appearance of new signals around 3690 cm^{-1} attributed to hydroxyl group (M-OH, and Ce-OH).

[0054] The surface area measurement (Figure 11) of the WOx-RhOx/$CeO_{2\text{-}200}$ bimetallic based catalyst indicated a surface of ca. 160 m^2/g. It should be noted that the surface area decreased (ca. 20 % loss) by the grafting as well as the different thermal treatment. Nevertheless, the surface area remains relatively high.

Example A2-b: Grafting of $[W_2(O^tBu)_6]$ on RhOx-CeO_2 through SOMC approach : (WOx-RhOx/CeO_2) (Rh 1.0; W 2.5)

[0055] A mixture of $[W_2(O^tBu)_6]$ (120 mg) and ROx_x-$CeO_{2\text{-}200}$ (2.15 g) was stirred in toluene for 15 h, at room temperature. The $[W_2(O^tBu)_6]/RhO_x$-$CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0056] The material of $[W_2(O^tBu)_6]/RhO_x$-$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst (WOx-RhOx/CeO_2) (Rh 1.0; W 2.5).

Example A2-c: Grafting of $[W(O)(O^tBu)_4]$ on RhOx-CeO_2 through SOMC approach : (WOx-RhOx/CeO_2) (Rh 1.0; W 2.0)

[0057] A mixture of $[W(O)(O^tBu)_4]$ (150 mg) and ROx_x-$CeO_{2\text{-}200}$ (2 g) was stirred in toluene for 15 h, at room temperature. The $[W(O)(O^tBu)_4]/RhO_x$-$CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0058] The material $[W(O)(O^tBu)_4]/RhO_x$-$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst (WOx-RhOx/CeO_2) (Rh 1.0; W 2.0).

Example A2-d: Grafting of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ on RhOx-CeO_2-ZrO_2 through SOMC approach : (WOx-RhOx/CeO_2-$ZrO_{2(200)}$) (Rh 1.0; W 2)

[0059] A mixture CeO_2-$ZrO_{2(200)}$ (6.10 g) and a desired amount of tetra-rhodium dodecacarbonyl as a dark-red crystalline solid (115 mg to reach *ca.* 1 wt% of Rh) was stirred at 25 °C in toluene (20 ml) for 12 h. After filtration, the

solid $[Rh_4(CO)_{12}]$-CeO_2-$ZrO_{2-(200)}$ was heated at 60 °C under vacuum (10^{-5} mbar) in order to remove the unused complex and to promote the formation of isolated Rh/CeO_2-$ZrO_{2(200)}$ species. After calcination at 400 °C under dry air (15 h) (Figure 8 c), bands between 3400 and 3700 cm^{-1} attributed to different vibration mode of v(CeO-H) are observed - this portion of hydroxyl groups can be further functionalized by other organometallic to yield heterobimetallic catalyst on CeO_2-ZrO_2 support.

[0060] A mixture of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$ (120 mg) and $RhOx_x$-CeO_2-$ZrO_{2(200)}$ (2.15 g) was stirred in toluene for 15 h, at room temperature. The $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$-/$RhO_x$-$CeO_2$-$ZrO_{2(200)}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0061] The material of $[W(\equiv C^tBu)(CH_2{}^tBu)_3]$-$RhO_x/CeO_2$-$ZrO_{2(200)}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst (WOx-RhOx/CeO_2-$ZrO_{2(200)}$) (Rh 1.0; W 2).

Example A2-e: Grafting of $[V(O)(OEt)_3]$ on RhOx-CeO_2 through SOMC approach : (VOx-RhOx/CeO_2) (Rh 1.0; V 2.0)

[0062] A mixture of $[V(O)(OEt)_3]$ (30 mg) and ROx_x-CeO_{2-200} (1.6 g) was stirred in toluene for 5 h, at room temperature. The $[V(O)(OEt)_3]/RhO_x$-CeO_{2-200} material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0063] The material $[V(O)(OEt)_3]/RhO_x$-CeO_{2-200} was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst (VOx-RhOx/CeO_2) (Rh 1.0; V 2.0).

Example A2-f: Grafting of [Nb(OEt)$_5$] on RhOx-CeO$_2$ through SOMC approach (NbOx-RhOx/CeO$_2$) (Rh 1.0; Nb 1.8)

[0064] A mixture of [Nb(OEt)$_5$] (70 mg) and ROx$_x$-CeO$_{2\text{-}200}$ (1.6 g) was stirred in toluene for 5 h, at room temperature. The [Nb(OEt)$_5$]/RhO$_x$-CeO$_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0065] The material [Nb(OEt)$_5$]/RhO$_x$-CeO$_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst (NbOx-RhOx/CeO$_2$) (Rh 1.0; Nb 1.8).

Part B: Preparation of bimetallic WOx-MOx/CeO$_2$ (M = V, Nb, Fe) catalysts through SOMC approach

Preparation Example B1: Preparation of WOx-CeO$_2$ through SOMC approach : WOx-CeO$_2$ (W 1.0)

[0066] A mixture of CeO$_{2(200)}$ (8.46 g) and a desired amount of W(≡C^{t}Bu)(CH$_2$^{t}Bu)$_3$ as yellow crystalline solid (241 mg to reach *ca.* 1 wt% of W) was stirred at 25 °C in toluene (20 ml) for 12 h. After filtration, the solid was heated at 60 °C under vacuum (10^{-5} mbar) in order to remove the unused complex and to promote the formation of isolated W/ CeO$_2$ species.

[0067] In addition to creating an additional anchoring site, the material obtained in the first step was calcined at 400°C and rehydrated by addition of vapor pressure of water. The sample was heated at 100 °C for 6 h in the presence of the moisture. Afterwards, the material was dehydroxylated under high vacuum (10^{-5} Torr) at 200 °C, and the excess as well as the physisorbed water were removed leading to WO$_x$-CeO$_{2\text{-}200}$.

[0068] Similar experiments were carried out for the preparation of the catalysts WOx/CeO2 with different loading (0.87, 1.74, 2, 3.7).

Example B2-a: Preparation of WOx-VOx/CeO_2 through SOMC approach: WOx-VOx/CeO_2 (W 1.0, V 0.8)

[0069] A mixture of $VO(OEt)_3$ (76 mg) and WO_x-$CeO_{2\text{-}200}$ (2.34 g) was stirred in toluene for 4 h, at room temperature. The VO(OEt)3/WO_x-$CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0070] The material of [W(≡C^{t}Bu)($CH_2{}^t$Bu)$_3$]-RhO_x-$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst (WOx-VOx/CeO_2), (W 1.0; V 0.8).

Example B2-b: Preparation of WOx-FeOx/CeO_2 through SOMC approach: WOx-FeOx/CeO_2 (W 1.0, Fe 0.6)

[0071] A mixture of Fe_2(1,3,5-Ph)$_4$ (65 mg) and WO_x-$CeO_{2\text{-}200}$ (2.14 g) was stirred in toluene for 4 h, at room temperature. The Fe_2(1,3,5-Ph)$_4$/WO_x-$CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0072] The material of Fe_2(1,3,5-Ph)$_4$/WO_x-CeO_2 was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst WOx-FeOx/CeO_2 (W 1.0; Fe 0.6).

Example B2-c: Preparation of WOx-NbOx/CeO_2 through SOMC approach: WOx-NbOx/CeO_2 (W 1.0; Nb 1.2)

[0073] A mixture of $Nb(OEt)_5$ (72 mg) and WO_x-$CeO_{2\text{-}200}$ (1.73 g) was stirred in toluene for 4 h, at room temperature. The $Nb(OEt)_5$/WO_x-$CeO_{2\text{-}200}$

material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0074] The material of $Nb(OEt)_5$-RhO_x-$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst WOx-NbOx/CeO_2 (W 1.0; Nb 1.2).

Part C: Preparation of bimetallic VOx-MOx/CeO_2 (M = Fe, Cu) catalysts through SOMC approach

Preparation Example C1: Preparation of VOx-CeO_2 through SOMC approach : VOx-CeO_2 (V 0.8)

[0075] A mixture $CeO_{2\text{-}200}$ (6.5 g) and a desired amount of $V(O)(OEt)_3$ (217 mg) was stirred at 25 °C in toluene (20 ml) for 12 h. After filtration, the solid was heated at 60 °C under vacuum (10^{-5} mbar) in order to remove the unused complex and to promote the formation of isolated V/CeO_2 species.

[0076] In addition to creating an additional anchoring site, the material obtained in the first step was calcined at 500°C and rehydrated by addition of vapor pressure of water. The sample was heated at 100 °C for 6 h in the presence of the moisture. Afterwards, the material was dehydroxylated under high vacuum (10^{-5} Torr) at 150 °C, and the excess as well as the physisorbed water were removed leading to VO_x-$CeO_{2\text{-}200}$ (V 0.8).

[0077] A similar experiment was carried out for the preparation of the catalysts VOx/CeO_2 with loading 2.1.

Example C2-a: Preparation of VOx-FeOx/CeO_2 through SOMC approach: VOx-FeOx/CeO_2 (V 0.8; Fe 0.5)

[0078] A mixture of $Fe_2(1,3,5\text{-}Ph)_4$ (56 mg) and VO_x-$CeO_{2\text{-}200}$ (2.06 g) was stirred in toluene for 4 h, at room temperature. The $Fe_2(1,3,5\text{-}Ph)_4$-WO_x/ $CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0079] The material of $Fe_2(1,3,5\text{-}Ph)_4$-WO_x/$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst VOx-FeOx/CeO_2 (V 0.8; Fe 0.5).

Example C2-b (Comparative): Preparation of VOx-CuOx/CeO_2 through SOMC approach: VOx-CuOx/CeO_2 (V 0.8; Cu 0.4)

[0080] A mixture of $[Cu(1,3,5\text{-}Ph)]_4$ (78 mg) and VO_x-$CeO_{2\text{-}200}$ (2.14 g) was stirred in toluene for 15 h, at room temperature. The $[Cu(1,3,5\text{-}Ph)]_4$-WO_x/ $CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0081] The material of $[Cu(1,3,5\text{-}Ph)]_4$-WO_x/$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst VOx-CuOx/CeO_2 (V 0.8; Cu 0.4).

Part D: Preparation of bimetallic NbOx-MOx/CeO_2 (M = Fe, Cu) catalysts through SOMC approach

Preparation Example D1: Preparation of NbOx-CeO_2 through SOMC approach : NbOx-CeO_2 (Nb 1.2)

[0082] A mixture $CeO_{2\text{-}200}$ (6.4 g) and a desired amount of $Nb(OEt)_5$ (268 mg) was stirred at 25 °C in toluene (20 ml) for 12 h. After filtration, the solid was heated at 60 °C under vacuum (10^{-5} mbar) in order to remove the unused complex and to promote the formation of isolated Nb/ CeO_2 species.

[0083] In addition to creating an additional anchoring site, the material obtained in the first step was calcined at 500°C and rehydrated by addition of vapor pressure of water. The sample was heated at 100 °C for 6 h in the presence of the moisture. Afterwards, the material was dehydroxylated under high vacuum (10^{-5} Torr) at 150 °C, and the excess as well as the physisorbed water were removed leading to NbO_x-$CeO_{2\text{-}200}$ (Nb 1.2).

[0084] Similar experiments were carried out for the preparation of the catalysts NbOx/CeO_2 with different loading (1.8; 3.4).

Example D2-a: Preparation of NbOx-FeOx/CeO_2 through SOMC approach: NbOx-FeOx/CeO_2 (Nb 1.2; Fe 0.6)

[0085] A mixture of $Fe_2(1,3,5\text{-}Ph)_4$ (58 mg) and VO_x-$CeO_{2\text{-}200}$ (1.85 g) was stirred in toluene for 15 h, at room temperature. The $Fe_2(1,3,5\text{-}Ph)_4$-NbO_x/ $CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0086] The material of $Fe_2(1,3,5\text{-}Ph)_4$-NbO_x/$CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h, leading to the catalyst NbOx-FeOx/CeO_2 (Nb 0.8; Fe 0.6).

Example D2-b (Comparative): Preparation of NbOx-CuOx/CeO_2 through SOMC approach: NbOx-FeOx/CeO_2 (Nb 1.2; Cu 0.4)

[0087] A mixture of $[Cu(1,3,5\text{-}Ph)]_4$ (78 mg) and NbO_x-$CeO_{2\text{-}200}$ (2.14 g) was stirred in toluene for 15 h, at room temperature. The $[Cu(1,3,5\text{-}Ph)]_4$-$NbO_x/CeO_{2\text{-}200}$ material was washed three times with toluene via filtration-condensation cycles. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-5} Torr).

[0088] The material of $[Cu(1,3,5\text{-}Ph)]_4$-$WO_x/CeO_{2\text{-}200}$ was calcined using a glass reactor under continuous flow of dry air at 500 °C for 16 h leading to the catalyst NbOx-CuOx/CeO_2 (V 0.8; Cu 0.4).

Catalytic activity test conditions

[0089] Pellet samples of approximately 33 mg were prepared under 1 ton pressure and put into a quartz reactor (diameter 4.5mm). A mixture of gas consisting of NO 300ppm, NH_3, 350ppm, O_2 10%, H_2O, 3%, CO_2 10%, He (balance), was sent through a catalytic bed at the rate of 300 mL/min. The reactor was heated from room temperature to 600°C with a heating rate of 10 °C/ min. The system was kept at 600°C for 10 min before cooling down to room temperature. Gas composition at the outlet was monitored during the heating up and cooling down by a combination of FTIR and GC-MS.

Claims

1. Process for preparing a catalyst material, comprising the steps of:

(a) providing a support material having surface hydroxyl (OH) groups, wherein the support material is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof;

(b) reacting the support material having surface hydroxyl (OH) groups of step (a) with a first precursor compound containing a metal element;

(c) heating the material obtained in step (b), having a grafted metal element, in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

(d) regenerating surface hydroxyl (OH) groups on the material obtained in step (c);

(e) reacting the support material having surface hydroxyl (OH) groups of step (d) with a second precursor compound containing a metal element different to the metal element of the first precursor compound;

(f) heating the material obtained in step (e), having grafted metal elements from both the first and second precursor compounds, in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour, so as to prepare a catalyst material,

wherein one of the first and second precursor compounds is a compound (L) containing a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W), and the other precursor compound is a compound (R) containing a metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt.

2. Process according to claim 1, wherein the support material provided in step (a), and/or the support material obtained by regeneration in step (d), contain(s) at least 0.3 mmol and at most 2.0 mmol OH groups/g of the support

material, and preferably at least 0.5 mmol and at most 1.3 mmol OH groups/g of the support material.

3. Process according to claim 1 or 2, wherein the compound (L) is:

(A) a compound containing at least one alkoxy or phenoxy group bound though its oxygen atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W); or

(B) a compound containing at least one hydrocarbon group bound though a carbon atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W).

4. Process according to claim 3, wherein the compound (A) containing at least one alkoxy or phenoxy group bound though its oxygen atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W) is at least one compound selected from the group consisting of: $[Nb(OEt)_5]_2$; $Nb(OAr)_5$ where Ar is the 1,3,5-trimethylphenyl $(CH_3)_3C_6H_2$- group; $[W{=}O(OEt)_4]_2$; $[W(O)(O^tBu)_4]$; $[W_2(O^tBu)_6]$; $[V(=O)(OEt)_3]_2$; $[V(=O)(O^iPr)_3]$; and $[Ta(OEt)_5]_2$.

5. Process according to claim 3, wherein the compound (B) containing at least one hydrocarbon group bound though a carbon atom to a metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W) is at least one compound selected from the group consisting of: $W(=NR)(=CH^tBu)_2(CH_2{}^tBu)_2$ (R = alkyl or aryl); $W(=O)(CH_2{}^tBu)_3Cl$; $W(\equiv C^tBu)(CH_2{}^tBu)_3$; $[(^tBuCH_2)_3W]O$; $[(^tBuCH_2)_3W{=}O]_2(\mu\text{-}O)$; $[^tBuO_3W{=}O]_2(\mu\text{-}O)$; $(^tBuO)_3W{\equiv}W(^tBuO)_3$; $Mo(=O)(CH_2{}^tBu)_3Cl$; $Mo(O)_2Mesityl_2$; $V(=O)Mes_3$; $V(=O)CH_2SiMe_3$; $Ta(=CH^tBu)(CH_2{}^tBu)_3$.

6. Process according to any of claims 1 to 5, wherein the compound (R) is a compound having alkyl, aryl, alkenyl and/or carbonyl groups bound to the metal element selected from the group consisting of: Ru, Rh, Ir, Pd, Mn, Fe and Pt.

7. Process according to claim 6, wherein the compound (R) is selected from the group consisting of: $Rh(\eta^3\text{-allyl})_3$; $Rh_4(CO)_{12}$; $Fe(Mesityl)_2$; $Fe(CO)_5$; $Mn(CH_2{}^tBu)_2$; $Me_5CpPtMe_4$; $Pd(dba)_2$; $Pd(COD)(CH_2SiMe_3)_2$; CpPdMe; $Pt(COD)Me_2$.

8. Process according to any of claims 1 to 7, wherein the compound (R) contains rhodium (Rh) or iron (Fe).

9. Process according to any of claims 1 to 8, wherein compound (L) contains one or more of: tungsten (W), niobium (Nb) and vanadium (V).

10. Process according to claim 9, wherein compound (L) contains tungsten (W).

11. Process according to any of claims 1 to 10, wherein the calcined catalyst material obtained by step (f) has at least 0.5 wt% and at most 9.0 wt%, preferably at least 1.0 wt% and at most 6.0 wt%, of metal element from Group 5 (V, Nb, Ta) or Group 6 (Cr, Mo, W).

12. Process according to any of claims 1 to 11, wherein the calcined catalyst material obtained by step (f) has at least 0.5 wt% and at most 6.0 wt%, preferably at least 1.0 wt% and at most 6.0 wt%, of metal element selected from the group consisting of: Ru, Mn, Fe, Rh, Ir, Pd and Pt.

13. Process for preparing a catalyst material, comprising the steps of:

(a) providing a support material having surface hydroxyl (OH) groups, wherein the support material is ceria (CeO_2), zirconia (ZrO_2) or a combination thereof;

(b) reacting the support material having surface hydroxyl (OH) groups of step (a) with a first precursor compound containing a metal element;

(c) heating the material obtained in step (b) having a grafted metal element in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

(d) regenerating surface hydroxyl (OH) groups on the heated material containing a grafted metal element obtained in step (c);

(e) reacting the support material having surface hydroxyl (OH) groups of step (d) with a second precursor compound;

(f) heating the material obtained in step (e) in an oxygen-containing atmosphere at a temperature of least 300°C, for at least 1 hour;

wherein one of the first or second precursor compounds contains tungsten (W) and the other precursor compound contains vanadium (V) or niobium (Nb), and wherein the calcined catalyst material obtained by step (f) has at least 0.6 wt% and at most 1.4 wt% of tungsten (W), and either at least 0.8 wt% and at most 1.6 wt% of niobium (Nb) or at least 0.5 wt% and at most 1.1 wt% of vanadium (V).

14. Process according to claim 13, wherein the calcined catalyst material obtained by step (f) has at least 0.8 wt% and at most 1.2 wt% of tungsten (W), and either at least 1.0 wt% and at most 1.4 wt% of niobium (Nb) or at least 0.6 wt% and at most 1.0 wt% of vanadium (V).

15. Process according to claim 13 or 14, wherein the calcined catalyst material obtained by step (f) has at least 0.9 wt% and at most 1.1 wt% of tungsten (W), and either at least 1.1 wt% and at most 1.3 wt% of niobium (Nb) or at least 0.7 wt% and at most 0.9 wt% of vanadium (V).

16. Process according to any of claims 13 to 15, wherein the first and second precursor compounds are:

(A) a compound containing at least one alkoxy or phenoxy group bound though its oxygen atom to V, Nb or W; or

(B) a compound containing at least one hydrocarbon group bound though a carbon atom to V, Nb or W.

17. Process according to claim 16, wherein compound (A) is at least one compound selected from the group consisting of: $[Nb(OEt)_5]_2$; $Nb(OAr)_5$ where Ar is the 1,3,5-trimethylphenyl $(CH_3)_3C_6H_2$- group; $[W{=}O(OEt)_4]_2$; $[W(O)(O^tBu)_4]$; $[W_2(O^tBu)_6]$; $[V(=O)(OEt)_3]_2$; $[V(=O)(O^iPr)_3]$.

18. Process according to claim 16, wherein compound (B) is at least one compound selected from the group consisting of: $W(=NR)(=CH^tBu)_2(CH_2{}^tBu)_2$ (R = alkyl or aryl); $W(=O)(CH_2{}^tBu)_3Cl$; $W(\equiv C^tBu)(CH_2{}^tBu)_3$; $[(^tBuCH_2)_3W]O$; $[(^tBuCH_2)_3W{=}O]_2(\mu\text{-}O)$; $[^tBuO_3W{=}O]_2(\mu\text{-}O)$; $(^tBuO)_3W{\equiv}W(^tBuO)_3$; $V(=O)Mes_3$; $V(=O)CH_2SiMe_3$.

19. Catalyst material as may be obtained by the process according to any of claims 1 to 12 or by the process according to any of claims 13 to 18.

20. Use of the catalyst material according to claim 19 as an ammonia selective catalytic reduction (NH_3-SCR) catalyst for nitrogen oxides (NOx) reduction.

21. Use according to claim 20, wherein the catalytic reduction takes place at a temperature of at most 260°C, preferably at most 250°C, more preferably at most 230°C.

22. Use according to claim 20 or 21, wherein the catalytic reduction takes place at a temperature of at least 100°C, preferably at least 130°C.

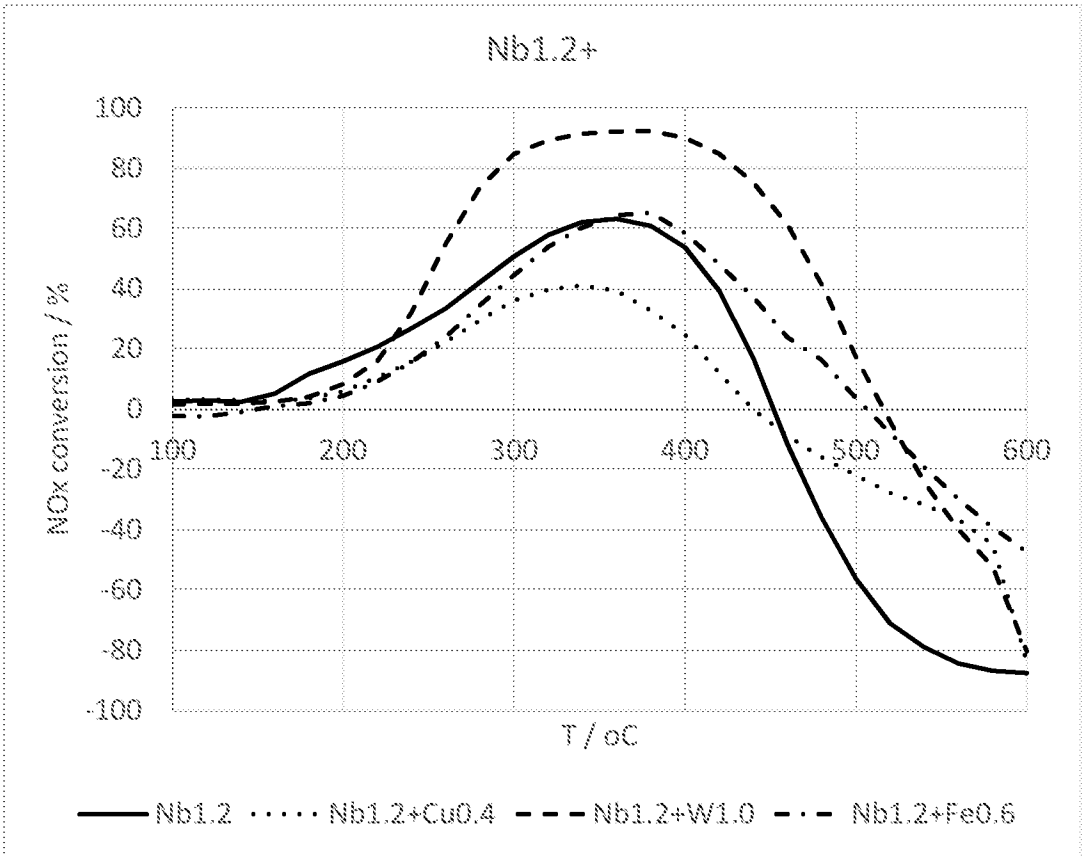

Nb1.2+
100
80
60
40
20
0
-20
-40
-60
-80
-100
NOx conversion / %
100
200
300
400
500
600
T / oC
Nb1.2
Nb1.2+Cu0.4
Nb1.2+W1.0
Nb1.2+Fe0.6

Figure 1

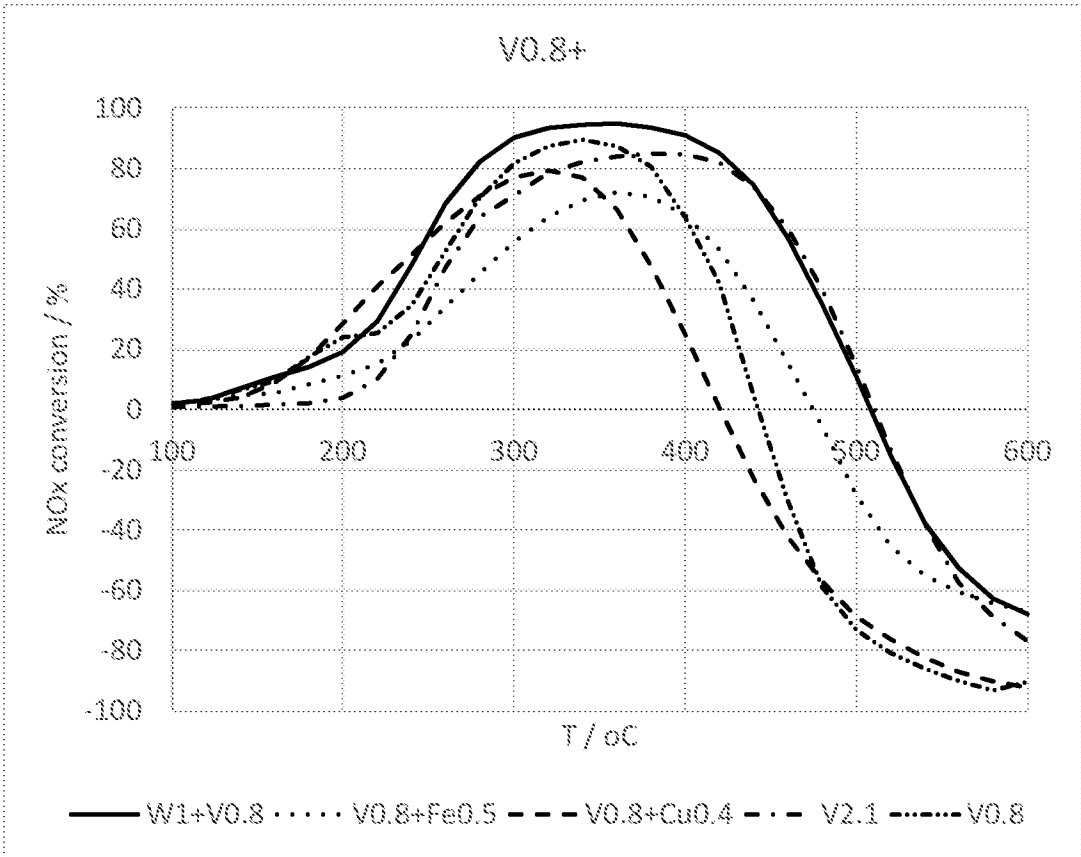

V0.8+
100
80
60
40
20
0
-20
-40
-60
-80
-100
NOx conversion / %
100
200
300
400
500
600
T / oC
W1+V0.8
V0.8+Fe0.5
V0.8+Cu0.4
V2.1
V0.8

Figure 2

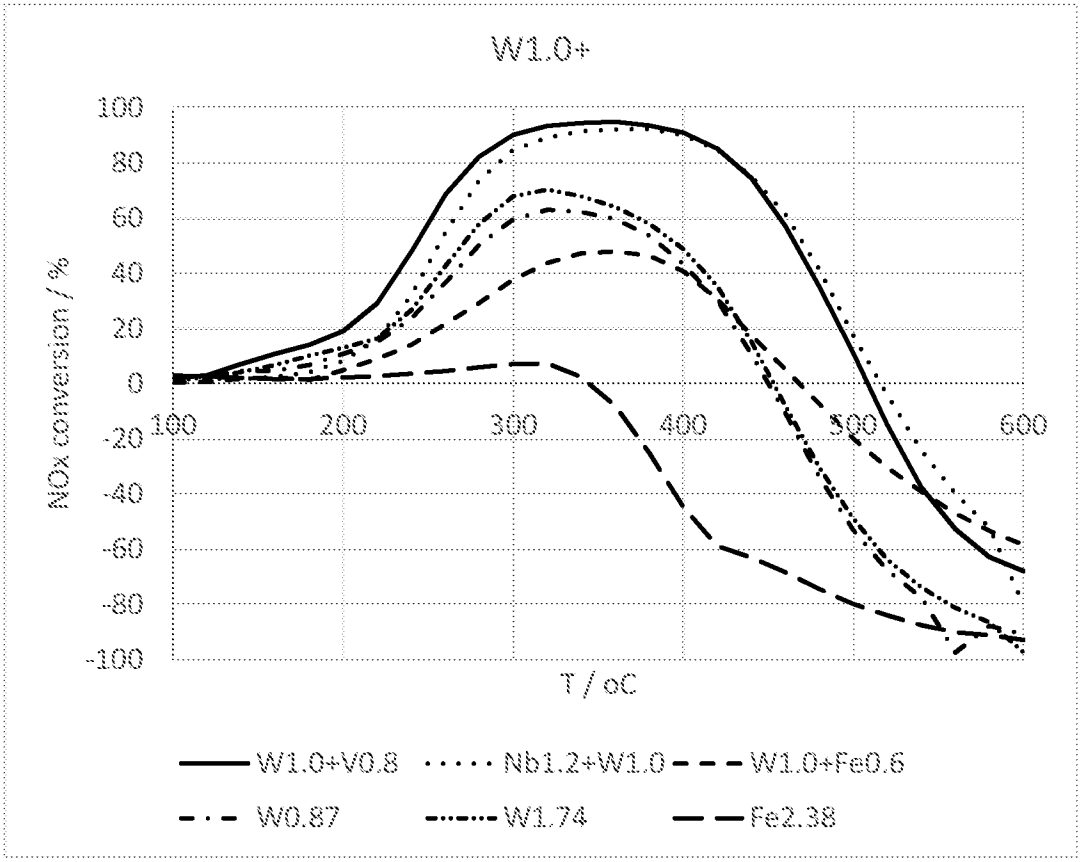

W1.0+
100
80
60
40
20
0
-20
-40
-60
-80
-100
NOx conversion / %
100
200
300
400
500
600
T / oC
W1.0+V0.8
Nb1.2+W1.0
W1.0+Fe0.6
W0.87
W1.74
Fe2.38

Figure 3

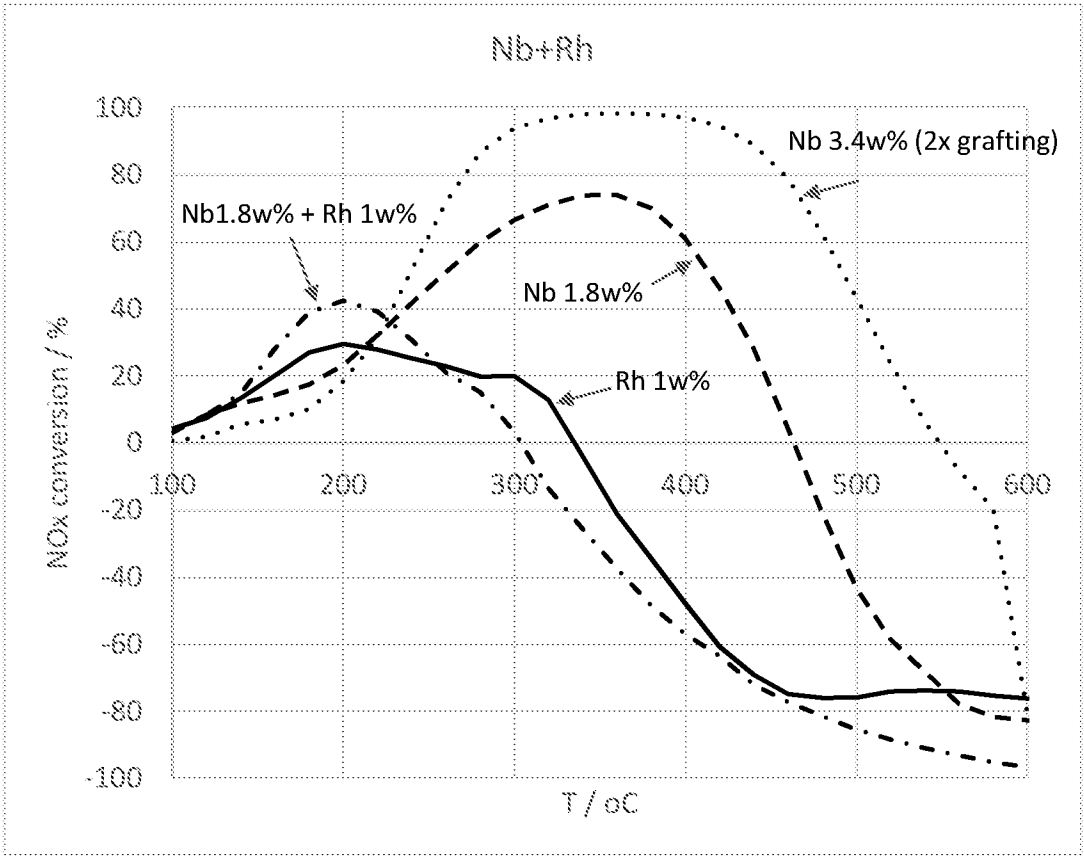

Nb+Rh
100
80
60
40
20
0
-20
-40
-60
-80
-100
100
200
300
400
500
600
NOx conversion / %
T / oC
Nb 3.4w% (2x grafting)
Nb1.8w% + Rh 1w%
Nb 1.8w%
Rh 1w%

Figure 4

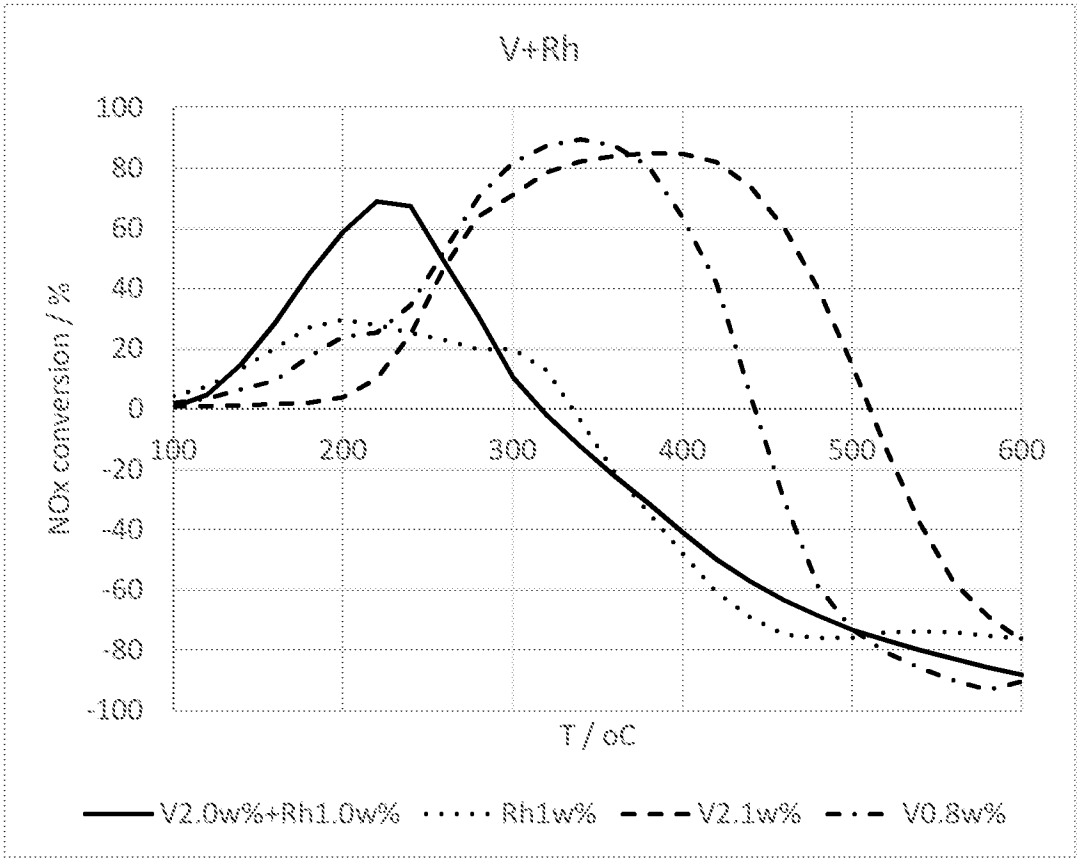

V+Rh
100
80
60
40
20
0
-20
-40
-60
-80
-100
100
200
300
400
500
600
NOx conversion / %
T / oC
V2.0w%+Rh1.0w%
Rh1w%
V2.1w%
V0.8w%

Figure 5

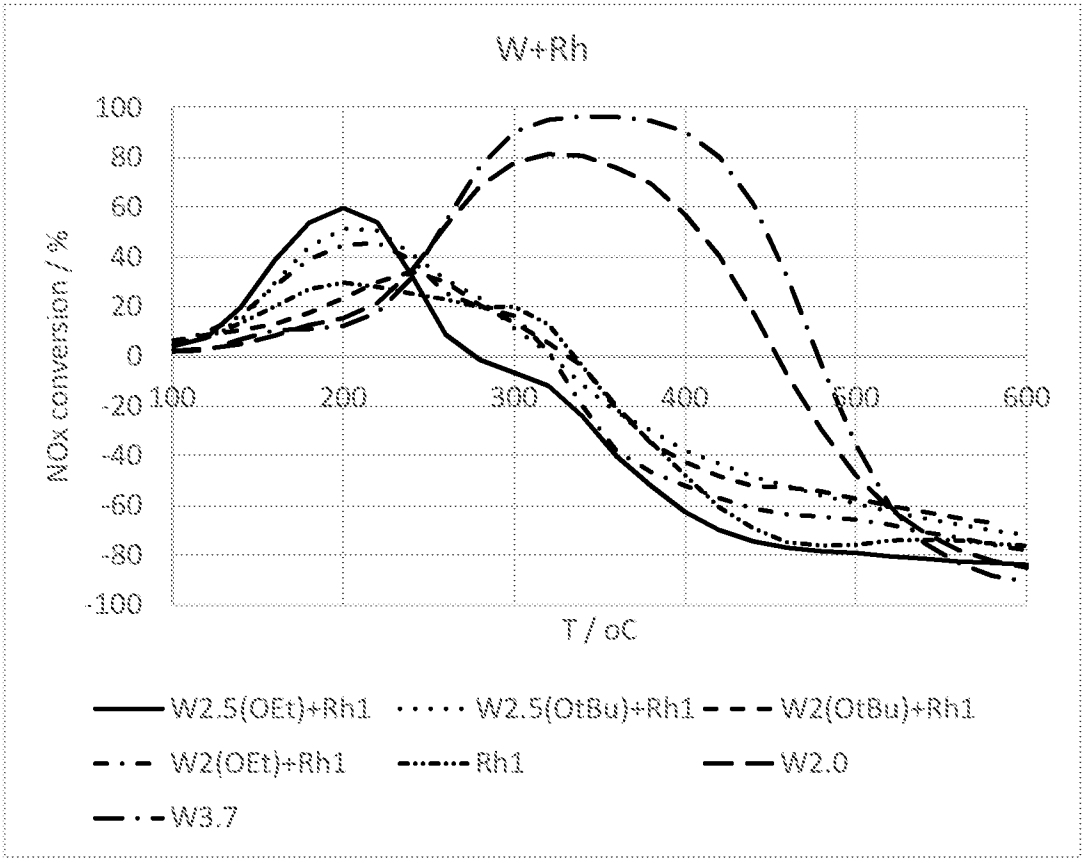

W+Rh
NOx conversion / %
T / oC
100
80
60
40
20
0
-20
-40
-60
-80
-100
100
200
300
400
500
600
W2.5(OEt)+Rh1
W2.5(OtBu)+Rh1
W2(OtBu)+Rh1
W2(OEt)+Rh1
Rh1
W2.0
W3.7

Figure 6

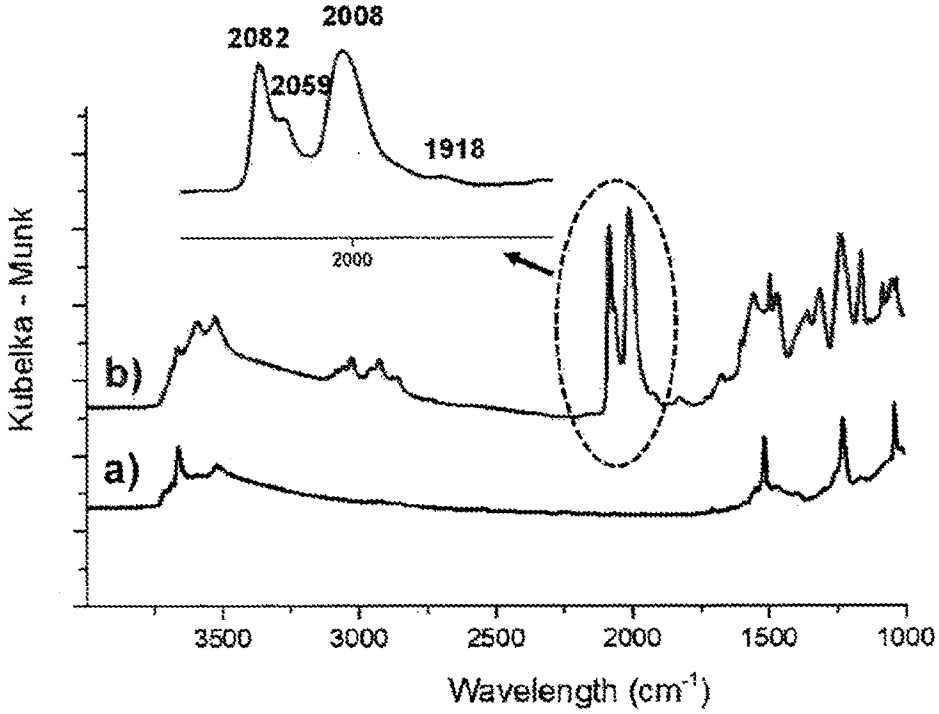

2082
2008
2059
1918
2000
b)
a)
Kubelka - Munk
3500
3000
2500
2000
1500
1000
Wavelength (cm-1)

Figure 7

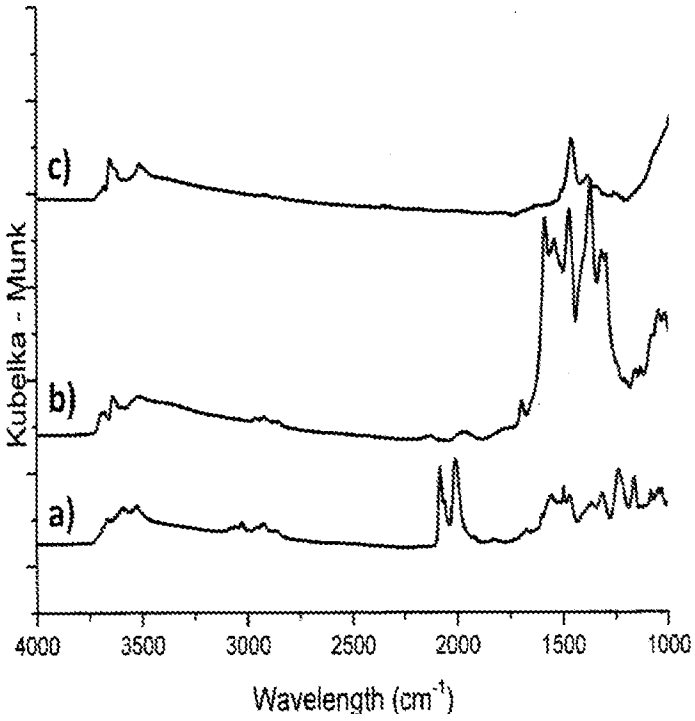


Figure 8

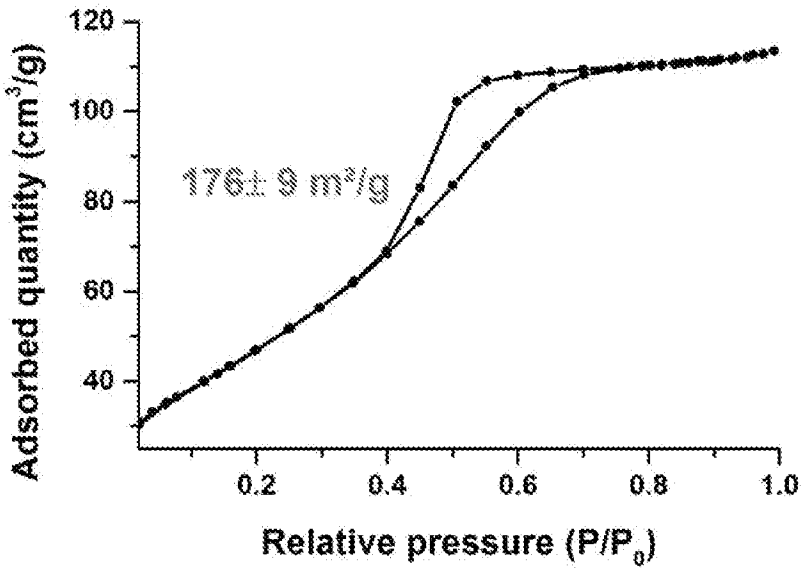


Figure 9

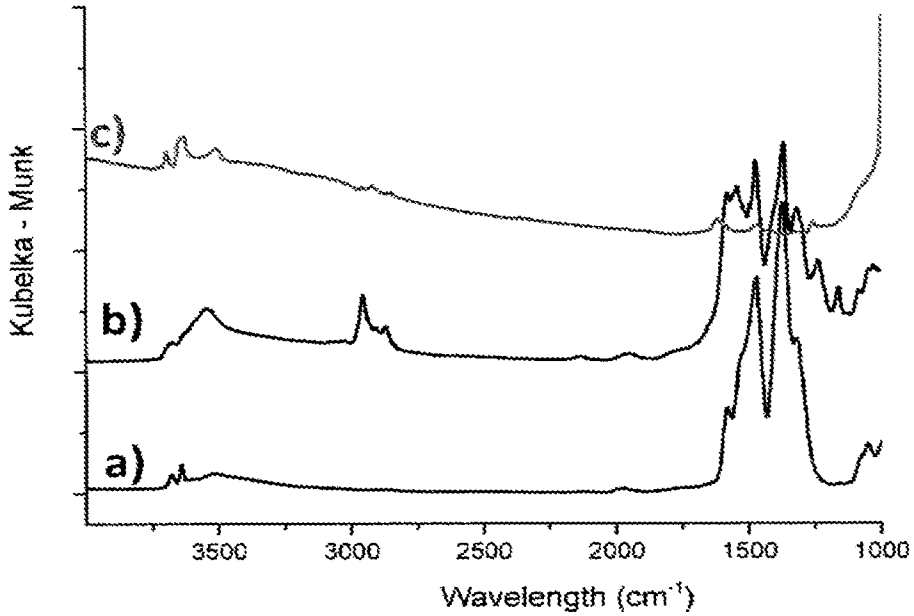


Figure 10

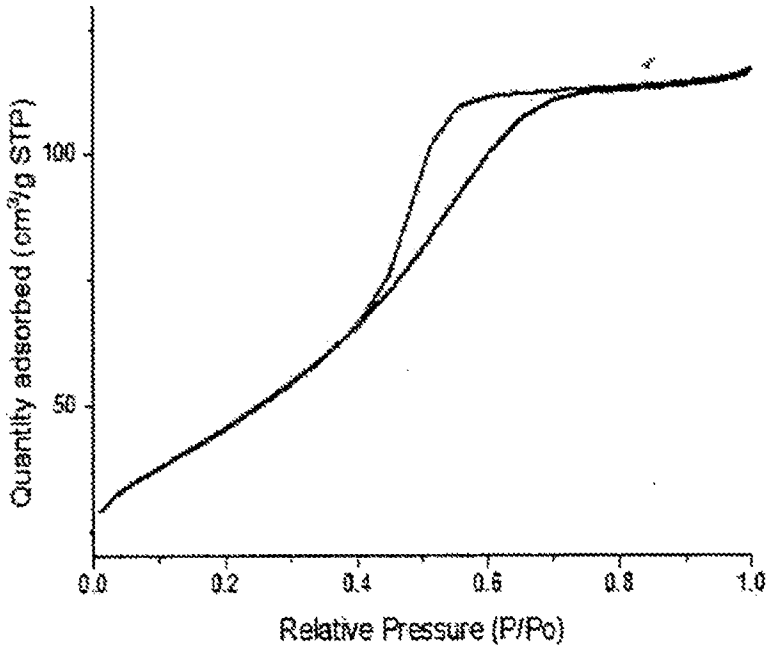


Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2021/000830

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/20 B01J23/28 B01J23/30 B01J23/648 B01J23/652
B01J23/847 B01J23/88 B01J23/887 B01J23/888 B01J35/00
B01J37/02 B01J37/08

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/069232 A1 (BASF CORP [US]) 11 April 2019 (2019-04-11)	19-22
A	claims; examples; tables	1-18

A	WO 2020/245620 A1 (TOYOTA MOTOR EUROPE [BE]; CENTRE NAT RECH SCIENT [FR] ET AL.) 10 December 2020 (2020-12-10) the whole document	1-22

A	WO 2020/245621 A1 (TOYOTA MOTOR EUROPE [BE]; CENTRE NAT RECH SCIENT [FR] ET AL.) 10 December 2020 (2020-12-10) the whole document	1-22

☐ 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	Date of mailing of the international search report
1 July 2022	11/07/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	de Cauwer, Robby

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2021/000830

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2019069232 A1	11-04-2019	BR 112020006411 A2	24-09-2020
		CN 111372678 A	03-07-2020
		EP 3691782 A1	12-08-2020
		JP 2020535960 A	10-12-2020
		KR 20200051816 A	13-05-2020
		US 2020290022 A1	17-09-2020
		WO 2019069232 A1	11-04-2019
WO 2020245620 A1	10-12-2020	CN 114340790 A	12-04-2022
		EP 3980179 A1	13-04-2022
		WO 2020245620 A1	10-12-2020
WO 2020245621 A1	10-12-2020	CN 114450087 A	06-05-2022
		EP 3980180 A1	13-04-2022
		WO 2020245621 A1	10-12-2020