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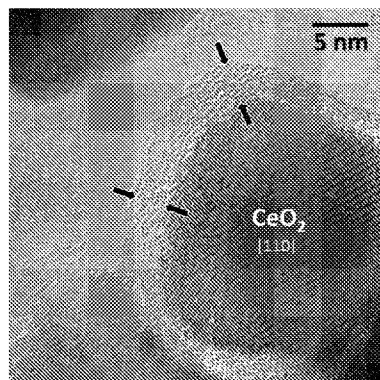
(54) Title: CATALYSTS BASED ON PD/CEO₂ AND PREPARATION METHOD THEREOF

FIG. 8b

(57) Abstract: The invention provides a Pd-ceria catalyst and a method for its preparation. The method involves the dry low energy milling of palladium and/or of a solid organic salt of palladium and ceria-containing support. The materials so obtained are comprised of ceria particles surrounded by an amorphous Pd-ceria mixed shell and are found to be highly active for catalytic methane oxidation. The catalysts prepared following the disclosed method are more active than the corresponding Pd-ceria formulations obtained by conventional incipient wetness impregnation.



“Catalysts based on Pd/CeO₂ and preparation method thereof”

DESCRIPTION

The invention provides a Pd-ceria catalyst for the oxidation of methane and/or VOC and a method for its preparation.

BACKGROUND

5 The recent concerns over the abundant emission of greenhouse gases from motor vehicles have pushed towards the development of more efficient catalyst systems.

In particular, for natural gas fueled vehicles there is the need for the design of catalytic systems with higher activity at low temperature and more resistant to deactivation in operating conditions. These issues are
10 becoming more and more important due to the exponential growth of the market of such vehicles. Catalysts used for the after-treatment of methane from exhaust gases or for methane conversion in general are usually comprised by a support oxide and a noble metal, which acts as the active phase.

15 In the literature, the palladium-ceria system is indicated as one of the most active for the catalytic combustion of methane (EP830199 and FR2546770) and its application is widely spread, alone or in combination with other metals or supports. In these systems, the noble metal is usually deposited onto the support oxide surface starting from a Pd-containing
20 solution, whether it is by the co-precipitation method, wet deposition or incipient wetness impregnation (IWI). The IWI method is the current state-of-the-art procedure, as it leads to a catalyst with a nice and uniform dispersion of palladium oxide in small clusters onto the ceria surface after calcination. The disadvantages of these syntheses are connected to the
25 use of solvents or acid solutions, used to promote the uniform distribution of noble metal onto the support, which have to be stocked, disposed of and after-treated when in the vapor form.

However, it would be highly desirable to reduce the environmental impact of catalysts manufacturing processes, e.g. by cutting off the use of solvents and/or by limiting the number of synthesis steps.

The mechanochemical approach is regarded as a very promising methodology to cope with these requests, even if the high number of controlling parameters hinders its widespread use in the catalyst industry. Despite there being some applications, this technology is far from being largely implemented at industrial level because disadvantages still exist. For instance, some materials obtained by the mechanochemical approach do not show better catalytic performances compared to their impregnated counterparts (Ismagilov Z.R. et al., *Catal Today*, **2010**, 157, 217-222), while in other publications the catalysts are highly active but require longer milling times and higher energies (Borchers C. et al., *J Nanopart Res*, **2016**, 18, 344, Kamolphop U. et al., *ACS Catal*, **2011**, 1, 1257-1262 and EP2040835), for example with the use of planetary mills, high ball-to-powder weight ratios and milling times of the order of few hours.

In other methods, there is the need for additives and subsequent thermal treatments, sometimes in combination with high energies.

In view of the considerations reported above, it is still strongly felt the need of developing a process for the preparation of a Pd-ceria catalyst system suitable for the catalytic oxidation of methane and/or VOC, said process having low environmental impact, thereby not involving the use of solvents, and being of simple industrial implementation.

Moreover, the catalytic activity of the catalyst system obtained/obtainable by the process should preferably be at least comparable to the catalytic activity of Pd-ceria catalysts obtained with IWI method.

The present invention solves the needs above reported by providing a mechanochemical process to produce a core-shell Pd-ceria catalyst system comprising dry grinding at least one selected among palladium metal, a solid palladium compound and mixtures thereof, with at least one Ce-based compound selected among ceria, ceria-based mixed oxides and

mixtures thereof, under mild grinding conditions (fast and low energy milling, at ambient temperature).

The Applicant has surprisingly found that the Pd-ceria catalyst system obtained/obtainable by the process of the invention, wherein only solid starting materials are used, is characterized by a peculiar morphological structure wherein the core of ceria particles is surrounded by an

Remarkably, said catalyst system was found to be highly active for catalytic abatement of gaseous hydrocarbon, particularly methane, VOC, NOx and/or soot. In particular, the catalyst system is more active than Pd-ceria catalysts obtained by conventional incipient wetness impregnation of comparable Pd loading.

SUMMARY OF THE INVENTION

In a first aspect the present invention refers to a core-shell catalyst system, characterized in that

- the core comprises at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, said core comprising at least one particle having size of about 2-100 nm; and
- the shell comprises an amorphous phase comprising Pd and an oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, the shell having thickness of $\leq$ about 5 nm.

In a further aspect, the present invention refers to a method for the preparation of the core-shell catalyst system described above comprising a step (i) of dry grinding a mixture comprising at least one selected among metallic Pd, a solid organic salt of palladium and mixtures thereof, and at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof.

In a still further aspect, the present invention refers to the use of the core-shell catalyst system of the instant disclosure for the catalytic abatement of at least one selected among a gaseous hydrocarbon, preferably methane, a VOC, NOx, soot and mixtures thereof.

DESCRIPTION OF THE FIGURES

The present invention is described in detail even with the help of the following figures, in which:

Figure 1 reports the light-off curves for PdCe DS and PdCe IW;

Figure 2 reports the light-off curves for PdAcCe DS 10, PdAcCe DS 15
5 and PdCe IW;

Figure 3 reports the light-off curves for PdCZ75 DS and PdCZ75 IW;

Figure 4 reports the light-off curves for PdPtCe DS and PdPtCe IW; and

Figure 5 reports the light-off curves for CuPdCe DS and CuPdCe IW.

In Figures 1-5 the solid lines, closed symbols represent heating; dotted
10 lines, open symbols represent cooling.

Figure 6 reports the time-on-stream behavior of PdCe DS, PdAcCe DS 10
and PdCe IW in dry atmosphere.

Figure 7 reports the time-on-stream behavior of PdCe DS, PdAcCe DS 10
and PdCe IW in wet atmosphere.

15 Figure 8a and 8b report HRTEM images of different portions of PdCe DS.

Figure 9 reports the EDX analysis of PdCe DS.

Figure 10 reports the HRTEM image of PdCeAc DS10.

Figure 11 reports the HRTEM image of PdOCe DS.

Figure 12 reports the HRTEM image of PdZr DS.

20 DETAILED DESCRIPTION

In the present description and in appended claims, the term “ceria” refers to cerium(IV) oxide of formula CeO_2 as well as to any non-stoichiometric, anion deficient form of ceria having formula $\text{CeO}_{(2-x)}$.

In the present description and in the appended claims, the term “ceria-based mixed oxide” refers to a cerium(IV) oxide or to a mixture of
25 Ce(IV)/Ce(III) oxide comprising at least one cation of a chemical element different from cerium.

In the context of the present invention, the term “solid” refers to chemicals which are solid at 25°C and 101,3 kPa.

30 In the context of the present invention, the term “dry grinding” refers to a crushing operation carried out in the absence of a solvent, i.e. wherein

only solid materials, preferably in powder form, are fed to the grinding apparatus.

In the context of the present invention, the amount of a metal in the catalyst system is expressed as wt.% of elemental metal with respect to the total weight of the catalyst system. It corresponds to the nominal load of the metal onto the catalyst system, the nominal load of a metal being the amount of metal added to (loaded onto) the catalyst system.

In the present description and appended claims the term "Volatile Organic Compound (VOC)" refers to any organic chemical compound whose composition makes it possible for it to evaporate at 25°C and 101.3 kPa.

In the context of the present invention, the term "gaseous hydrocarbons" refers to hydrocarbons which are in the gaseous state at 25°C and 101.3 kPa.

In a first aspect the present invention refers to a core-shell catalyst system, characterized in that

- the core comprises at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, said core comprising at least one particle having size of about 2-100 nm, preferably of about 5-100 nm, more preferably of about 20-80 nm; and
- the shell comprises an amorphous phase comprising Pd and an oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, the shell having thickness of $\leq$ about 5 nm, preferably of about 0,5 – 5 nm.

In one embodiment, the core may comprise ceria.

In one embodiment, the core may consist of at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, preferably the core may consist of ceria.

In one embodiment, the ceria-based mixed oxide may comprise (be doped with) $\leq$ about 40 mol.%, preferably about 1-40 mol.%, more preferably about 10–30 mol.%, of at least one element selected among Zr, In, Sn, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, preferably Zr.

The oxide comprised in the core of the catalyst system may have low or high surface area, preferably comprised in the range $\leq$ about 50 m²/g, more preferably about 0,5-50 m²/g, still more preferably about 2,0 – 30,0 m²/g.

- 5 The surface area of the oxide comprised in the core is measured using the BET method as described below, on the oxide (cerium oxide, cerium-based mixed oxide) in its powder form, after calcination, if any, and before milling with the noble metal.

In the core-shell catalyst system of the invention, the shell preferably
10 comprises the same oxide or oxides comprised in the core of the catalyst system.

In one embodiment, the size of the core may be equal to or greater than the thickness of the shell, preferably the size of the core may be greater than the thickness of the shell.

- 15 In one embodiment, the shell may comprise $\leq$ about 5,0 wt.% of Pd, preferably $\leq$ about 2,0, more preferably $\leq$ about 1,5 wt.%, still more preferably about 0,1 – 1,0 wt.%, wherein the amount of Pd corresponds to the nominal load of Pd.

In a further embodiment, the shell may comprise at least one further metal
20 M selected among Cu, Ru, Rh, Ag, Os, Ir, Pt, Au and mixture thereof, preferably among Cu, Pt and mixtures thereof, more preferably it is Pt.

In one embodiment, the total metal loading of the catalyst system may be $\leq$ about 5,0 wt.%, preferably $\leq$ about 2,0 wt.%, more preferably $\leq$ about 1,5 wt.%, still more preferably about 0,1 – 1,0 wt.%, wherein the total metal
25 loading is the sum of the weights of the metals loaded onto the catalyst system, including Pd, expressed as wt.% with respect to the weight of the catalyst system.

TEM analysis performed on a series of samples showed that no metal is present inside the oxide core of the catalyst system, suggesting that all
30 loaded noble metal is found on the particles surface (i.e. in the shell).

Thus, the metal content of the shell corresponds to the nominal metal loading.

In one embodiment, the weight ratio Pd:M (metal(s)) may range from about 90:10 to about 10:90, preferably from about 70:30 to about 30:70,
5 more preferably the weight ratio Pd:M may be about 50:50.

The weight ratio refers to the ratio between the nominal loading of Pd and the nominal loading of the second metal M.

In one embodiment, the shell may consist of an amorphous phase comprising Pd and an oxide as described above.

10 In one embodiment, the shell may consist of an amorphous phase consisting of Pd and an oxide as described above.

In one embodiment, the Pd comprised in the shell may be selected among metallic Pd, an organic compound of Pd, an inorganic compound of Pd and mixtures thereof, said organic and inorganic compound being solid.

15 The Pd comprised in the shell may be selected among metallic Pd, an organic salt of Pd and mixtures thereof, more preferably may be selected among metallic Pd, $\text{Pd}(\text{CH}_3\text{COO})_2$ and mixtures thereof, more preferably may be metallic Pd.

When present, the further metal M comprised in the shell may be selected
20 among metallic M, a solid compound of metal M and mixtures thereof, preferably may be metallic M.

According to a preferred embodiment, the shell of the catalyst system of the invention may comprise metallic Pd and metallic Pt.

In a further aspect, the present invention refers to a method for the
25 preparation of the core-shell catalyst system described above comprising a step (i) of dry grinding a mixture comprising at least one selected among metallic Pd, a solid organic salt of palladium and mixtures thereof and at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof.

30 According to one embodiment, for the preparation of the core-shell catalyst system of the invention wherein the shell comprises a further

metal M, the method may comprise a further step (ii) of dry grinding the core-shell catalyst system obtained from step (i) with at least one selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M.

- 5 In one embodiment, for the preparation of the core-shell catalyst system wherein the shell comprises a further metal M, the mixture of step (i) may comprise at least one selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M.

In one embodiment, the mixture of step (i) may comprise at least one
10 selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M, and the method may comprise a further step (ii) as described above.

In one embodiment, said at least one further metal M may be selected among Cu, Ru, Rh, Ag, Os, Ir, Pt, Au and mixture thereof, preferably
15 among Cu, Pt and mixtures thereof, more preferably Pt.

In one embodiment, the total metal loading of the catalyst system may be $\leq$ about 5,0 wt.%, preferably $\leq$ about 2,0 wt.%, more preferably $\leq$ about 1,5 wt.%, still more preferably about 0,1 – 1,0 wt.%, wherein the metal loading is the sum of the weights of the metals, including Pd, loaded onto the
20 catalyst system in step (i) and in step (ii), if present, expressed as wt.% with respect to the weight of the catalyst system.

In one embodiment, the weight ratio Pd:M (metal(s)) may range from about 90:10 to about 10:90, preferably from about 70:30 to about 30:70, more preferably the weight ratio Pd:M may be about 50:50.

- 25 The weight ratio refers to the ratio between the nominal loading of Pd and the nominal loading of the second metal M.

In one embodiment, the amount of Pd in the mixture of the dry grinding step (i) may be $\leq$ about 5,0 wt.%, preferably $\leq$ about 2,0 wt.%, more preferably $\leq$ about 1,5 wt.%, still more preferably about 0,1 – 1,0 wt.%
30 (palladium nominal loading).

The Pd compound of step (i) may be selected among metallic Pd, $\text{Pd}(\text{CH}_3\text{COO})_2$ and mixtures thereof, preferably may be metallic Pd.

When present, the solid compound of the further metal M may be selected among an organic compound of M, an inorganic compound of M and
5 mixtures thereof.

In a preferred embodiment, the dry-grinding step (i) and/or (ii) may be carried out at temperature of about 20-35°C and pressure of about 101,3 kPa.

In one embodiment, the dry grinding step (i) and the dry grinding step (ii),
10 if present, may be carried out by ball-milling.

In one embodiment, the dry grinding step (i) and the dry grinding step (ii), if present, may be carried out using only one grinding ball.

In one embodiment, the weight ratio of grinding media to powders may be comprised in the range of about 5-20, preferably may be about 10. A
15 higher ball-to-powder weight ratio induces a noticeable worsening of the catalytic activity.

In one embodiment, the dry grinding step (i) and the dry grinding step (ii), if present, may be carried out for a time comprised of about 5-20 minutes. The Applicant has surprisingly found that milling times lower than 5
20 minutes gave unsatisfactory results as the contact between metal and support was insufficient to obtain an optimized shell layer, whereas longer milling time induces a noticeable worsening of the catalytic activity.

According to a preferred embodiment, the method for the preparation of the core-shell catalyst system may comprise a step (a) of calcining the at
25 least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, wherein step (a) is carried out before the dry grinding step (i). The calcining step (a) may be carried out in presence of oxygen, more preferably of air. In a further preferred embodiment, the calcining step (a) may be carried out at temperature $\geq$ about 850°C, preferably of
30 about 850° – 1200°C, more preferably of about 850°-1000°C, still more

preferably of about 900°C, for a time $\geq$ about 2 hours, preferably of about 2 – 4 hours, more preferably of about 3 hours.

In one embodiment, the at least one ceria-based mixed oxide used in the dry grinding step (i) may comprise (be doped with) $\leq$ about 40 mol.%,
5 preferably about 1-40 mol.%, more preferably about 10 – 30 mol.%, of at least one element selected among Zr, In, Sn, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, preferably Zr.

In one embodiment, the oxide of the dry grinding step (i) may have low or high surface area, preferably comprised in the range $\leq$ about 50 m²/g,
10 more preferably about 0,5-50 m²/g, still more preferably about 2,0 – 30,0 m²/g. The surface area of the oxide of the dry grinding step (i) is measured using the BET method as described below, on the oxide (cerium oxide, cerium-based mixed oxide) in its powder form, after calcination, if any, and before milling with the noble metal.

15 In one embodiment, the dry grinding step (i) and the dry grinding step (ii), if present, may be carried out under low energy milling. According to a preferred embodiment, the dry grinding steps (i) and (ii), if present, may be carried out in a ball-mill oscillating at a frequency of about 10-30 Hz, preferably of about 15 Hz.

20 Optionally, the raw materials used in the method of the invention may be pre-mixed without grinding to homogenize the powders mixture.

In a further aspect, the present invention refers to a core-shell catalyst system obtained/obtainable from the method as described above.

Via the method of the invention a new catalyst is formed, with unique
25 features and a higher catalytic activity compared to traditional Pd-ceria catalysts prepared by conventional wet methods.

The core-shell catalyst system of the invention is obtained/obtainable by a fast, low energy milling method without the need of solvents or any thermal treatment. The core-shell catalytic system of the invention has
30 proven to be highly active in catalytic abatement of noxious compounds.

Accordingly, in a further aspect the present invention refers to the use of the core-shell catalyst system as described above for the catalytic abatement of at least one compound selected among a gaseous hydrocarbon, preferably methane, a VOC, NO_x, soot and mixtures thereof.

- 5 In one embodiment, the use of the core-shell catalyst of the invention may be for the catalytic abatement of exhaust gas of a natural gas fueled engine.

The following examples are given in order to better illustrate the invention and are not intended to limit it in any way.

10 **EXAMPLES**

HRTEM: high resolution transmission electron microscopy was carried out with a JEOL 2010F electron microscope equipped with a field emission source at an accelerating voltage of 200 kV. The point-to-point resolution achieved was 0.19 nm and the resolution between lines was 0.14 nm.

- 15 Particle size: The size of the particles (oxide) comprised in the core was obtained from HRTEM images by averaging the dimensions (diameter) several hundred particles for each sample.

Shell thickness: the dimensions of the layer were directly measured over HRTEM images.

- 20 EDX analysis: EDX spectra were obtained over selected areas of the HRTEM images by using an electron beam at the nanoscale.

Surface area: the surface area were measured via Brunauer-Emmett-Teller (BET) method in a Micromeritics Tristar 2000 after sample evacuation at 423 K for 1,5 hours using N₂ as adsorptive at 77 K.

- 25 Amorphous phase of the shell: the amorphous nature of the shell was determined by the absence of lattice fringes in the HRTEM images.

- Dry grinding conditions: the dry grinding was carried out in a Pulverisette 23 Mini-Mill by grinding together dry powders of the components for a time comprised between 5 and 15 min at a frequency of 15 Hz. The grinding was carried out in a 15 ml zirconia bowl using 1 zirconia grinding ball (15 mm diameter, $\rho = 5,9 \text{ g cm}^{-3}$).
- 30

Catalytic test: Catalytic tests were carried out by placing 120mg of the catalyst system in a quartz micro-reactor on a quartz wool bed. The reactor was inserted in a tubular furnace to control the temperature and exposed to a mixture of 0.5 vol.% CH₄, 2 vol.% O₂ in He (dry atmosphere).

- 5 Two heating/cooling ramps were performed up to 900°C (10°C/min) and the conversion of methane was monitored with an on-line ABB Uras 14 IR gas analyzer.

Stability test: the stability of the samples was assessed during 24 h time-on-stream tests carried out at 450°C in dry (see above) or wet
10 atmosphere. In the latter case, 10 vol.% of water vapor was added to the dry feed. Prior to each stability test, a methane oxidation cycle (up to 900°C and back to room temperature) in dry atmosphere was carried out on 120 mg of sample as described above. After this cycle, the temperature was raised up to 450°C at 10°C/min for the stability test.

15 **Example 1**

The sample (PdCe DS) was prepared using the Fritsch Pulverizette 23 Mini-mill. Cerium oxide was obtained by calcinating commercial Ceroxid (Treibacher) at 900°C for 3 hours in air. 990 mg of cerium oxide powder was weighted and briefly mixed in a sample holder with 10 mg of
20 palladium black powder (Aldrich), until a homogeneous mix was formed. The powder was then put into the zirconia bowl, together with the grinding ball. The mini-mill was set to oscillate at 15 Hz for 10 minutes; afterwards, the obtained catalyst system was removed from the bowl by using a soft brush. The Pd nominal loading was 1 wt.%

25 **Example 2**

For the preparation of the sample (PdAcCe DS 10) the procedure follows the same steps as Example 1, differing only for the Pd precursor used. To have a final loading of 1wt.% of Pd, 21,1 mg of Pd(CH₃COO)₂ (Aldrich) were mixed with 990 mg of cerium oxide (previously calcined as in
30 Example 1) and milled 10 minutes at 15 Hz in the Pulverizette 23 Mini-mill.

Example 3

The sample (PdAcCe DS 15) was made by initially following the procedure of Example 2. The powders were milled for 10 minutes in the Pulverisette, removed and put in the grinding bowl again and milled for additional 5 minutes at 15 Hz. The two-step preparation helps avoiding cluttering of ceria particles and to improve Pd distribution on ceria surface.

Example 4

To prepare the sample (PdCZ75 DS), a procedure similar to Example 1 was used. $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (CZ75) support was obtained by co-precipitation, dried at 120°C for 16 hours and calcined at 900°C in air for 3 hours. 990 mg of CZ75 powders are measured and mixed with 10 mg of Pd black, then the same steps as Example 1 were followed.

Example 5

A bimetallic PtPdCe DS catalyst system was prepared with a weight ratio of Pt:Pd equal to 1. The total metal loading $(\text{Pd}+\text{Pt})/\text{wt}_{\text{cat}}$ was 1 wt.%. At first, 990 mg of ceria (previously calcined as in Example 1) were mixed with 5 mg of Pd black and milled for 10 minutes at 15 Hz. The powders were taken out of the bowl with a brush and mixed to 5 mg of metallic Pt (Aldrich). Then they are re-loaded into the zirconia bowl and milled for 10 minutes.

Example 6

A bimetallic catalyst system containing Pd and Cu was prepared following the same route as Example 5. The total metal loading $(\text{Pd}+\text{Cu})/\text{wt}_{\text{cat}}$ was 1 wt.%. Copper was added to the previously milled catalyst system in its metallic form (Aldrich).

Comparative examples 7-8

Catalysts were also prepared by conventional incipient wetness impregnation (IWI) technique on the same ceria support used in Example 1 (PdCe IW) and Example 4 (PdCZ75 IW). For the impregnation, an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (Aldrich, 99,99%) was used in appropriate amount to reach a nominal Pd loading of 1 wt%. The catalysts were then dried at 120°C overnight and calcined at 900°C for 3 hours in static air.

Comparative examples 9-10

Bimetallic catalysts were prepared by conventional IWI technique on the same ceria support as Example 5 (PtPdCe IW) and Example 6 (CuPtCe IW). For the impregnation, an aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (Aldrich, 99,99%) and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Strem, 99%) or $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich, 98%) was used in order to have a final metal loading of 0,5 wt% Pd and 0,5 wt% Pt (or 0,5 wt% Cu). The catalysts were then dried at 120°C overnight and calcined at 900°C for 3 hours in static air.

Comparative example 11

The catalyst sample PdOCe DS was prepared following the procedure of Example 1, using the same cerium oxide support and 11,6mg of palladium(II) oxide (Strem, 99,9%) to obtain a final metal loading of 1,0 wt.%Pd.

Comparative example 12

The catalyst sample PdZr DS was prepared following the procedure of Example 1 and 4, using zirconium oxide as support. The zirconium oxide powder (ZrO_2) was obtained by precipitation, dried at 120°C for 16 hours and calcined at 900°C in air for 3 hours.

Catalytic tests

The catalyst systems of Examples 1-6 and of Comparative examples 7-12 were subjected to the catalytic test. Table 1 summarizes the activation temperatures (T_{10} , i.e. temperature to achieve 10% methane conversion) and reaction rates (calculated at 270°C) for the different catalyst systems, together with their surface area and nominal palladium loading.

Sample	Nominal Pd loading (wt%)	Surface area (m ² /g)	T ₁₀ [K]	Reaction rate (μmol/g _{Pd} *s)
PdCe DS	1	3.2	564	33.0
PdAcCe DS 10	1	2.9	565	36.3
PdAcCe DS 15	1	3.1	578	20.6
PdCe IW	1	2.3	583	11.5
PdCZ75 DS	1	20.0	585	20.7
PdCZ75 IW	1	13.8	614	5.9
PtPdCe DS	0.5 (0.5 Pt)	4.9	608	35.3 ^[a,b]
PtPdCe IW	0.5 (0.5 Pt)	3.8	689	5.7 ^[a,b]
CuPdCe DS	0.5 (0.5 Cu)	5.3	697	7.3 ^[a,b]
CuPdCe IW	0.5 (0.5 Cu)	1.9	863	0 ^[a,b]
PdOCe DS	1	4.1	726	0 ^[b]
PdZr DS	1	5.2	613	8.4
PdZr IW	1	4.6	603	10.7

Table 1 - Pd loading, surface areas, activation temperatures and reaction rates for Pd-based catalysts.

^[a] Reaction rate is calculated per gram of metal, Pd+Pt or Pd+Cu;

5 ^[b] Reaction rate is calculated at T = 310°C.

The core-shell catalyst systems of Examples 1-6 made according to the method of the invention showed very good catalytic activity for methane oxidation.

10 The light-off curves of methane combustion for the Examples 1-6 and for Comparative examples 7-10 are shown in Figures 1-5.

The light-off curves present the shape typical of Pd-based catalyst systems in which a loss in methane conversion during cooling is observed due to the decomposition of PdO (which is formed during heating in excess oxygen). Remarkably, this feature is almost disappeared on catalysts systems PdAcCe DS10 and PdAcCe DS15 prepared using Pd acetate as metal precursor (Figure 2). All the samples prepared by the dry grinding method according to the invention show a much higher catalytic activity for methane oxidation compared to their impregnated counterparts.

This is evidenced clearly when looking at the values of T_{10} and reaction rates: the T_{10} are much lower for DS catalysts and their reaction rates are significantly higher than those of the corresponding IW samples.

Stability tests

- 5 The samples of Example 1 and 2 and of Comparative Example 7 were tested also for stability during time-on-stream operation in dry and wet atmosphere, and the results are shown in Figure 6 and 7, respectively.

It can be observed that in dry atmosphere both PdCe DS and PdAcCe DS retain almost completely their initial activity (decrease in methane
10 conversion of about 3%), while the IW sample loses around 9% of methane conversion, starting from a much lower value. In presence of water vapor (Figure 7) the catalysts suffer from higher deactivation. The PdCe DS sample is the more resistant to water poisoning in these conditions, losing only 13% of its initial activity, while PdCe IW decreases
15 by 25% starting from around the same conversion value. PdAcCe DS 10 shows a peculiar behavior: it starts from a much higher conversion value (around 80%), which rapidly falls to 50% in the first 6 hours; after that, the loss in activity is slower and it reaches 40% of its initial value by the end of the 24-hour isothermal period.

20 Characterization

Figures 8a and 8b show significant HRTEM images of PdCe DS. As it can be observed, most of the ceria crystallites are covered by an amorphous layer measuring between 2 and 5 nm in thickness. This amorphous shell is compact and perfectly defined following the perimeter of the ceria
25 particles. Interestingly, the ceria crystallites covered by this layer do not exhibit sharp edges; in most cases, they present a rounded morphology, which suggests that the dry grinding of Pd by mechanical mixing certainly affects the surface of the ceria crystallites.

EDX analysis (Figure 9) shows the common occurrence of cerium and
30 palladium, being the signal of Ce much more intense than that of Pd and indicating that the shell is comprised of a mixed Pd-Ce phase.

A thinner and less uniform shell appears when using Pd acetate instead of Pd black as metal precursor (Figure 10).

Figures 11 and 12 refers to catalyst systems prepared by dry grinding palladium oxide and ceria (PdOCe DS) or metallic palladium and zirconia (PdZr DS). These samples do not exhibit the core-shell structure characterizing the catalyst system of the invention.

CLAIMS

1. A core-shell catalyst system, characterized in that
 - the core comprises at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, said core comprising at least one particle having size of 2-100 nm, preferably of 5-100 nm, more preferably of 20-80 nm; and
 - the shell comprises an amorphous phase comprising Pd and an oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, the shell having thickness of ≤ 5 nm, preferably of 0,5 – 5 nm.
2. The core-shell catalyst system according to claim 1, wherein the core comprises ceria.
3. The core-shell catalyst system according to claim 1 or 2, wherein the ceria-based mixed oxide comprises ≤ 40 mol.%, preferably 1-40 mol.%, more preferably 10–30 mol.%, of at least one element selected among Zr, In, Sn, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, preferably Zr.
4. The core-shell catalyst system according to any one of claims 1-3, wherein the oxide comprised in the core has surface area measured by BET method comprised in the range ≤ 50 m²/g, preferably 0,5-50 m²/g, more preferably 2,0–30,0 m²/g.
5. The core-shell catalyst system according to any one of claims 1-4, wherein the shell comprises $\leq 5,0$ wt.% of Pd, preferably $\leq 2,0$ wt.%, more preferably $\leq 1,5$ wt.%, still more preferably 0,1 – 1,0 wt.%.
6. The core-shell catalyst system according to any one of claims 1-5, wherein the shell comprises at least one further metal M selected

among Cu, Ru, Rh, Ag, Os, Ir, Pt, Au and mixture thereof, preferably among Cu, Pt and mixtures thereof, more preferably Pt.

- 5 7. The core-shell catalyst system according to claim 6, wherein the total metal loading of the shell is $\leq 5,0$ wt.%, preferably $\leq 2,0$ wt.%, more preferably $\leq 1,5$ wt.%, still more preferably 0,1 – 1,0 wt.%.
- 10 8. The core-shell catalyst system according to claim 6 or 7, wherein the weight ratio Pd:M ranges from 90:10 to 10:90, preferably from 70:30 to 30:70, more preferably is 50:50.
- 15 9. The core-shell catalyst system according to any one of claims 6-8, wherein the further metal M comprised in the shell is selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M.
- 20 10. The core-shell catalyst system according to any one of claims 1-9, wherein the Pd comprised in the shell is selected among metallic Pd, an organic compound of Pd, an inorganic compound of Pd and mixtures thereof, preferably among metallic Pd, an organic salt of Pd, and mixtures thereof, more preferably among metallic Pd, Pd(CH₃COO)₂ and mixtures thereof, still more preferably is metallic Pd.
- 25 11. A method for preparing of the core-shell catalyst system as defined in claim 1, comprising a step (i)) of dry grinding a mixture comprising at least one selected among metallic Pd, a solid organic salt of palladium and mixtures thereof and at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof.

12. The method according to claim 11, wherein the Pd in the mixture of the dry grinding step (i) is $\leq 5,0$ wt.%, preferably $\leq 2,0$ wt.%, more preferably $\leq 1,5$ wt.%, still more preferably 0,1 – 1,0 wt.%.

5 13. The method according to claim 11 for the preparation of the core-shell catalyst system as defined in any one of claims 6-9, comprising a further step (ii) of dry grinding the core-shell catalyst system obtained from step (i) with at least one selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M.

10

14. The method according to claim 11 or 13 for the preparation of the core-shell catalyst system as defined in any one of claims 6-9, wherein the mixture of step (i) comprises at least one selected among metallic M, a solid compound of metal M and mixtures thereof, preferably metallic M.

15

15. The method according to claim 13 or 14, wherein the total metal loading of the shell is $\leq 5,0$ wt.%, preferably $\leq 2,0$ wt.%, more preferably $\leq 1,5$ wt.%, still more preferably 0,1 – 1,0 wt.%.

20

16. The method according to any one of claims 13-15, wherein the weight ratio Pd:M in the shell ranges from 90:10 to 10:90, preferably from 70:30 to 30:70, more preferably is 50:50.

25

17. The method according to any one of claims 11-13, wherein the dry grinding step (i) and the dry grinding step (ii), if present, is carried out by ball-milling.

18. The method according to claim 17, wherein the dry grinding step (i) and the dry grinding step (ii), if present, is carried out with a weight ratio of grinding media to powders of 5-20.
- 5 19. The method according to any one of claims 11-18, wherein the dry grinding step (i) and the dry grinding step (ii), if present, is carried out for a time comprised between 5 and 20 minutes.
- 10 20. The method according to any one of claims 11-19, comprising a step (a) of calcining at least one oxide selected among ceria, a ceria-based mixed oxide and mixtures thereof, wherein step (a) is carried out before the dry grinding step (i).
- 15 21. The method according to claim 20, wherein the calcining step (a) is carried out in presence of oxygen, more preferably of air.
- 20 22. The method according to claim 20 or 21, wherein the calcining step (a) is carried out at temperature $\geq 850^{\circ}\text{C}$, preferably of 850°C – 1200°C , more preferably of 850°C – 1000°C , still more preferably of 900°C , for a time ≥ 2 hours, preferably of 2 – 4 hours, more preferably of 3 hours.
- 25 23. The method according to any one of claims 11-22, wherein the at least one ceria-based mixed oxide of the dry grinding step (i) comprises ≤ 40 mol.%, preferably 1-40 mol.%, more preferably 10 – 30 mol.%, of an element selected among Zr, In, Sn, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, preferably Zr.
- 30 24. Use of the core-shell catalyst system as described in any one of claims 1-10 for the catalytic abatement of at least one selected among a gaseous hydrocarbon, preferably methane, a VOC, NO_x, soot and mixtures thereof.

25. The use according to claim 24 of the core-shell catalyst system for the catalytic abatement of exhaust gas of a natural gas fueled engine.

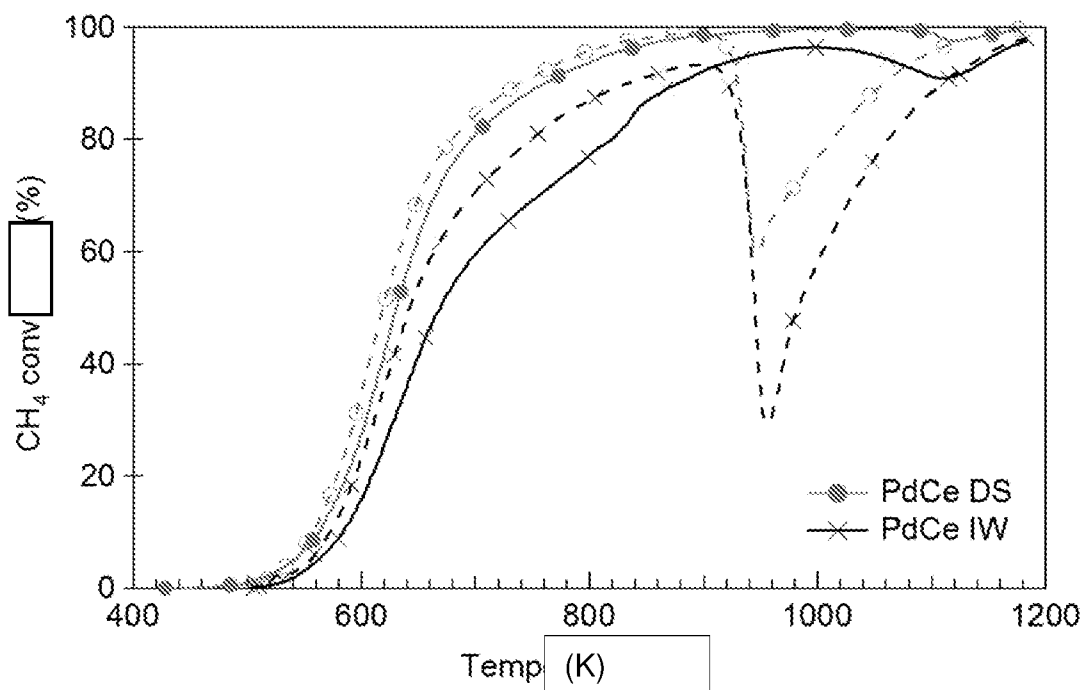


FIG. 1

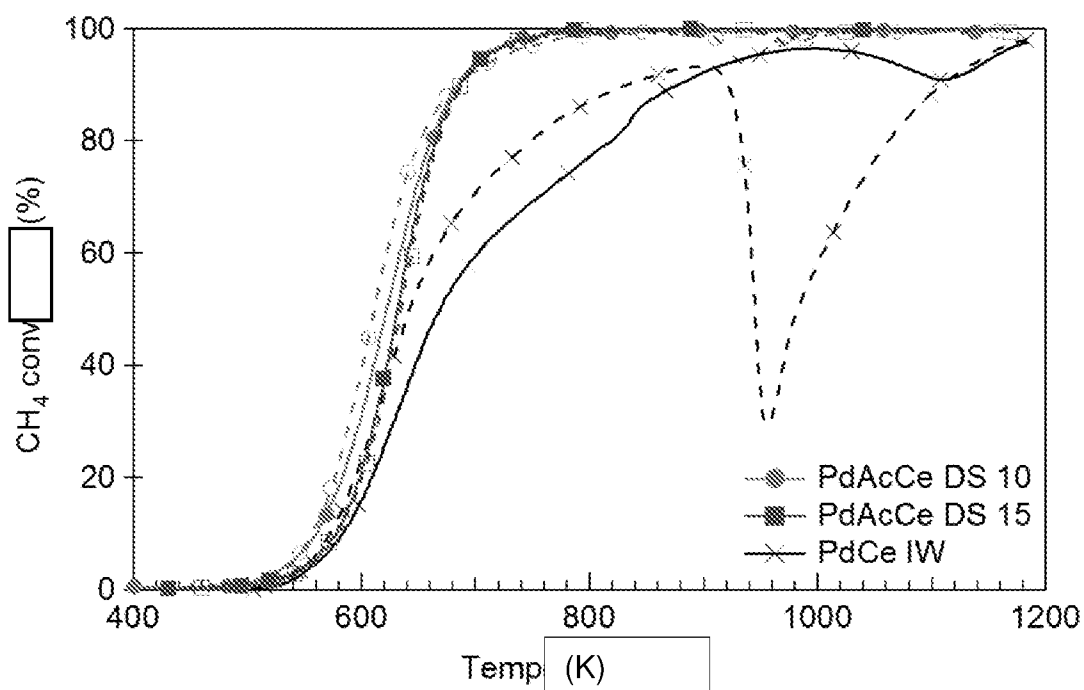


FIG. 2

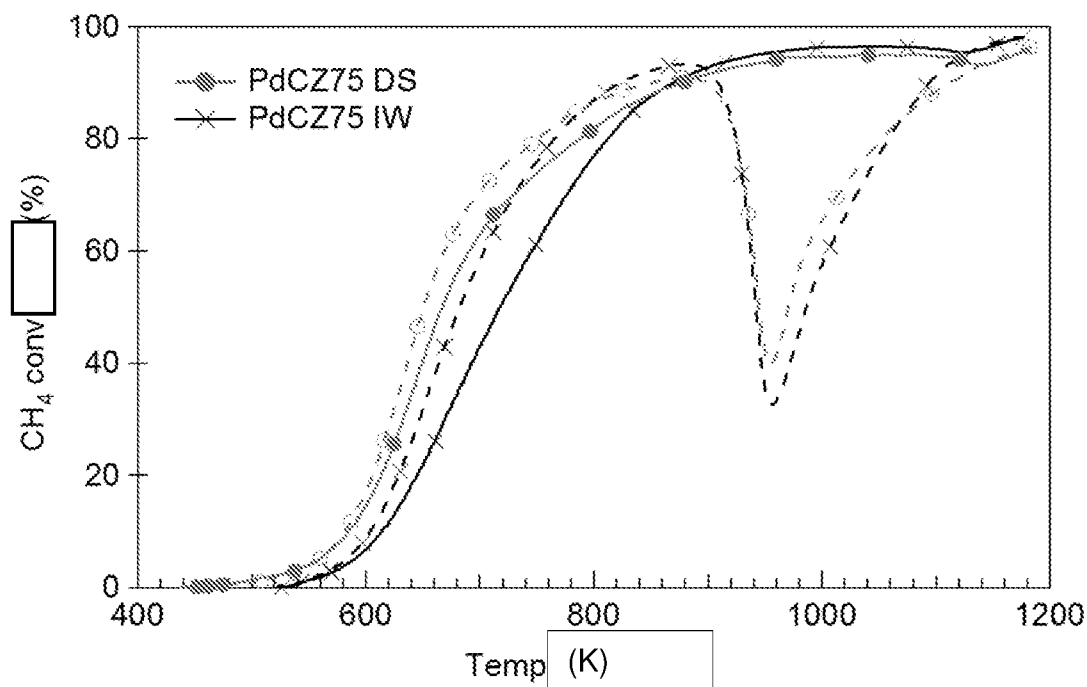


FIG. 3

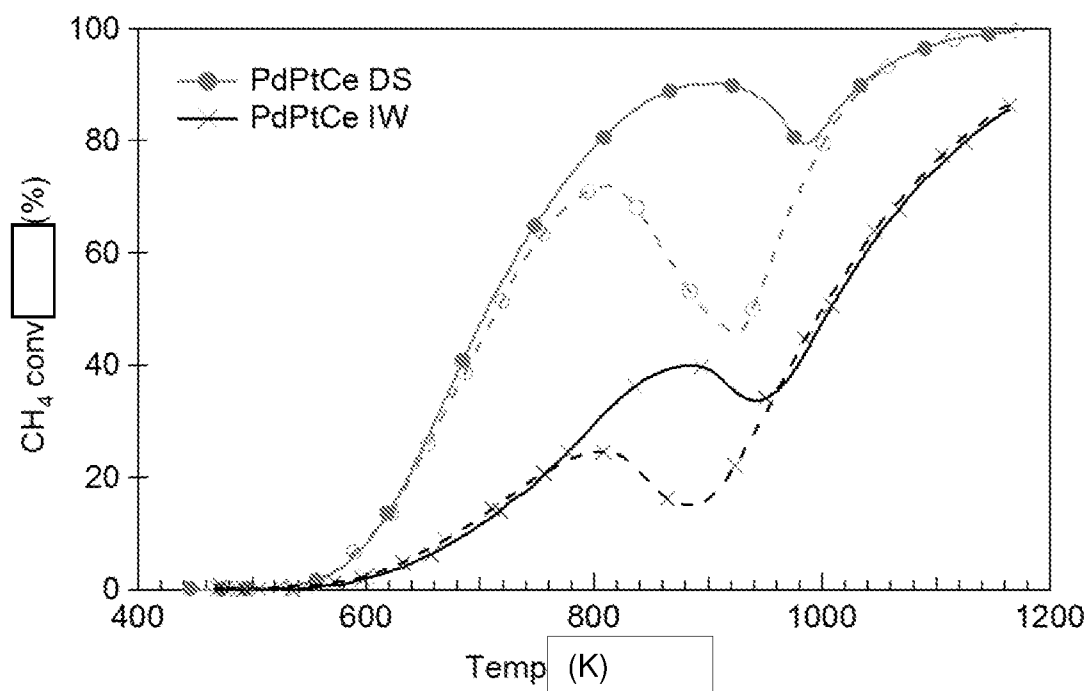


FIG. 4

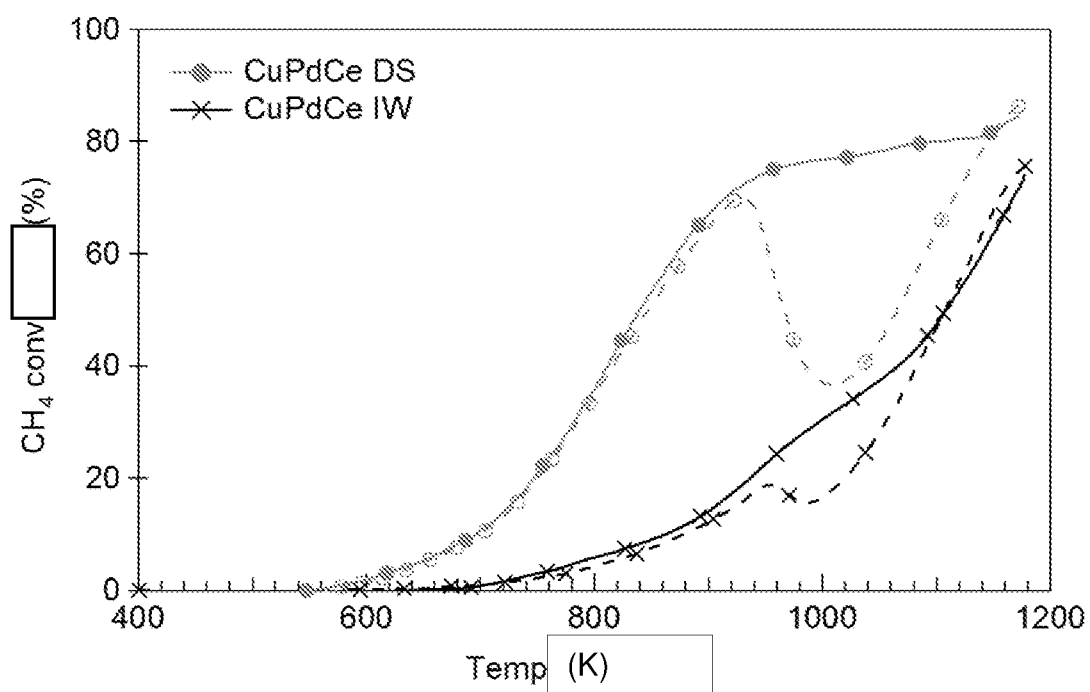


FIG. 5

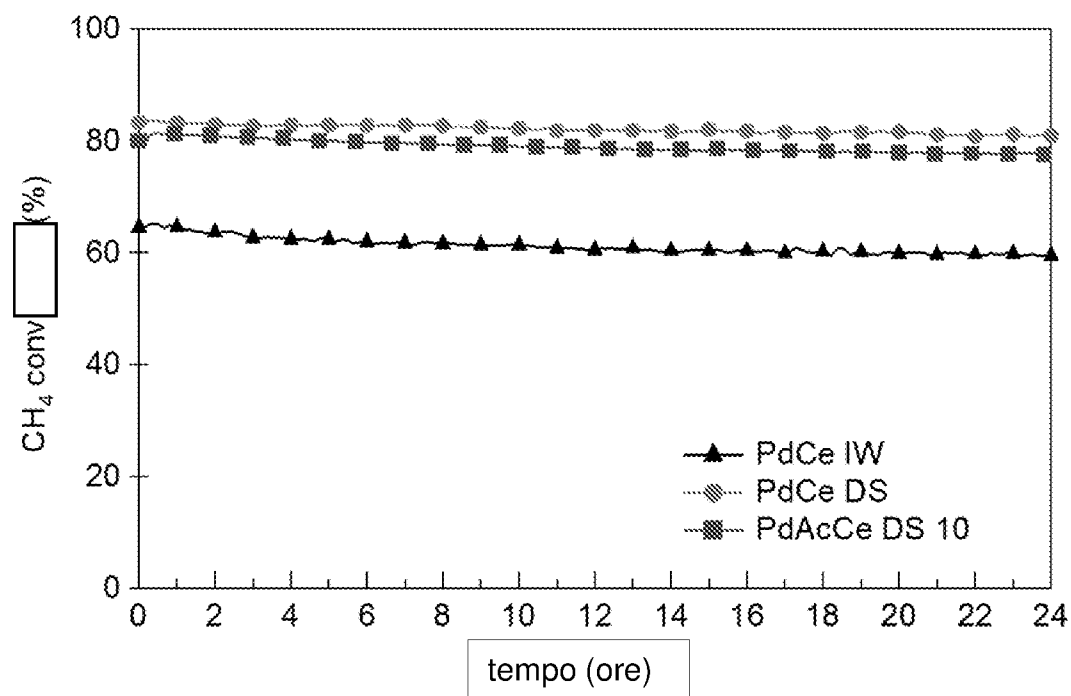


FIG. 6

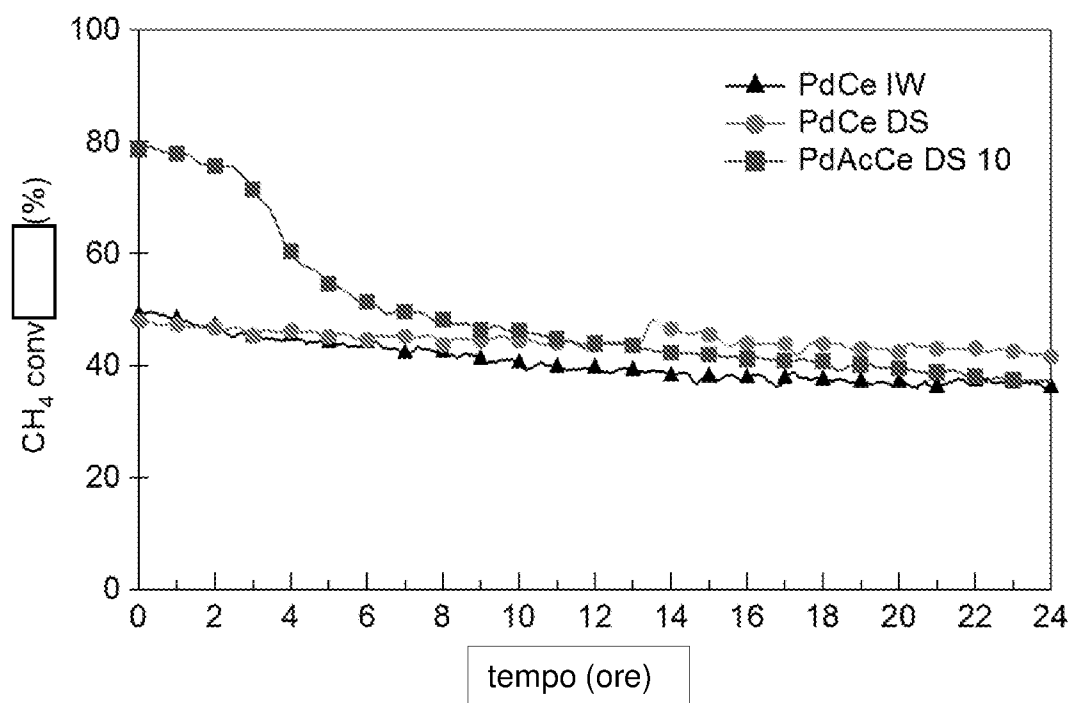


FIG. 7

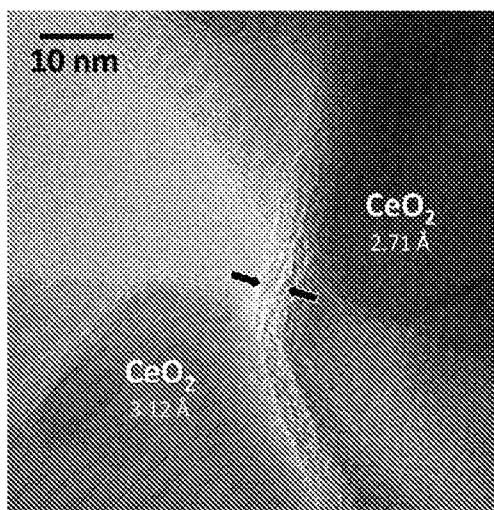


FIG. 8a

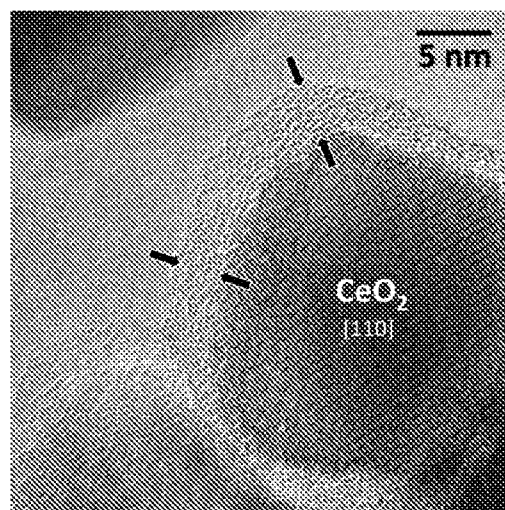


FIG. 8b

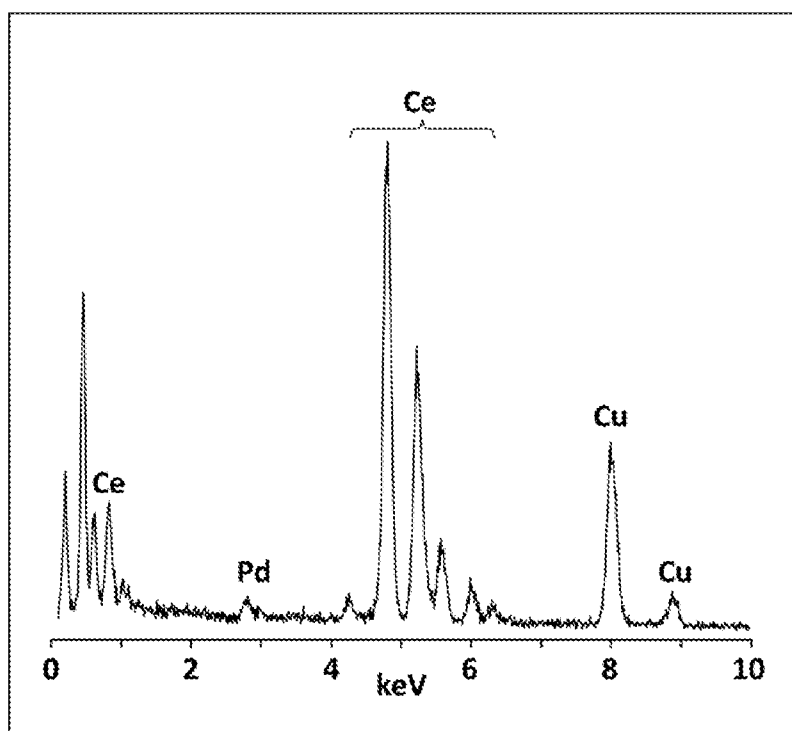


FIG. 9

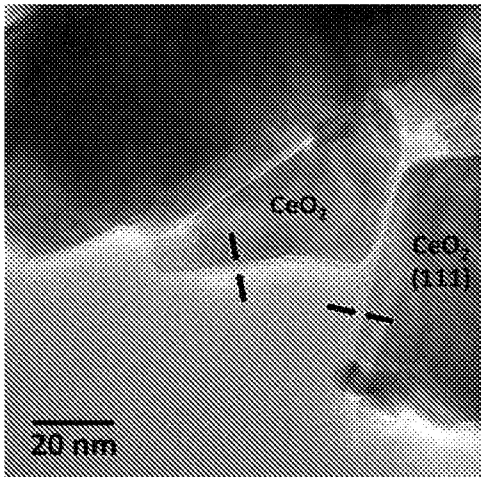


FIG. 10

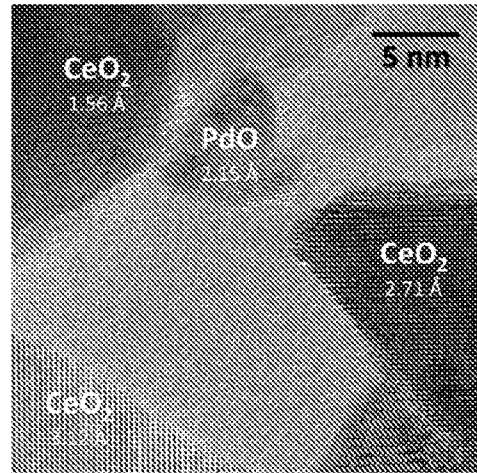


FIG. 11

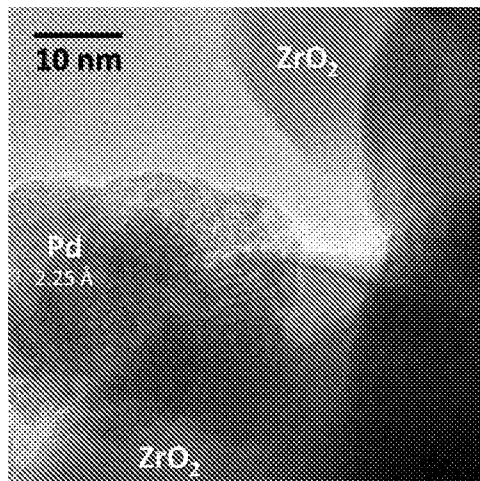


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054583

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01J23/63 B01J13/04	B01J23/00 B01J37/08
	B01J23/89 B01D53/86	B01J35/00 B01J37/00
		B01J35/10
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B01J B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JIN JIANHUI ET AL: "Solid-State Method Toward PdO-CeO ₂ Coated Monolith Catalysts for Oxygen Elimination Under Excess Methane", CATALYSIS LETTERS, SPRINGER NEW YORK LLC, UNITED STATES, vol. 144, no. 12, 14 September 2014 (2014-09-14), pages 2052-2064, XP035903449, ISSN: 1011-372X, DOI: 10.1007/S10562-014-1366-6 [retrieved on 2014-09-14] par. "Experimental" table 1 figures 1,7	1-25
X	WO 2016/127430 A1 (UNIV TIANJIN [CN]) 18 August 2016 (2016-08-18) abstract ----- -/-	1-25
☒ 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 2 October 2018		Date of mailing of the international search report 11/10/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Omegna, Anna

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054583

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& EP 3 257 815 A1 (UNIV TIANJIN [CN]) 20 December 2017 (2017-12-20) abstract figures 1,7,8 claims 1,2 paragraphs [0005], [0009] paragraph [0020] - paragraph [0022] paragraph [0024] table 4 example 14	
A	----- DONG QIANG ET AL: "Aluminium doped ceria-zirconia supported palladium-alumina catalyst with high oxygen storage capacity and CO oxidation activity", MATERIALS RESEARCH BULLETIN, vol. 48, no. 12, 21 May 2013 (2013-05-21), pages 4989-4992, XP028736934, ISSN: 0025-5408, DOI: 10.1016/J.MATERRESBULL.2013.05.054 abstract par. "Experimental"	1-25
A	----- WO 03/101612 A2 (JOHNSON MATTHEY PLC [GB]; AIELLO RITA [US]; ANDERSEN PAUL JOSEPH [US]) 11 December 2003 (2003-12-11) examples	1-25
A	----- MAJD AL-NAJI ET AL: "Mechanochemical preparation of advanced catalytically active bifunctional Pd-containing nanomaterials for aqueous phase hydrogenation", CATALYSIS SCIENCE & TECHNOLOGY, vol. 5, no. 4, 1 January 2015 (2015-01-01), pages 2085-2091, XP055511546, United Kingdom ISSN: 2044-4753, DOI: 10.1039/C4CY01174K par. "Experimental section" -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/054583

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016127430 A1	18-08-2016	CN 107207274 A	26-09-2017
		EP 3257815 A1	20-12-2017
		US 2018029012 A1	01-02-2018
		WO 2016127430 A1	18-08-2016

WO 03101612 A2	11-12-2003	AU 2003241011 A1	19-12-2003
		US 2005081443 A1	21-04-2005
		WO 03101612 A2	11-12-2003
