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Pd catalysts supported on silicon nitride for the combustion of methane: Influence of the crystalline and amorphous phases of the support and of the preparation method on the catalytic performances

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Abstract

Non-oxide refractory materials, such as silicon nitride having high thermal stability and thermal conductivity can be used as catalytic supports. The influence of the Si_3N_4 support nature and of the chemical compounds used for preparations on the physical-chemistry and catalytic properties of the palladium systems in the total oxidation of methane was investigated. A strong influence of the phase composition and the crystalline state of supports on the catalytic properties in the total oxidation of methane of the Pd catalysts was found. The activity of Pd catalysts increases with the α-Si_3N_4 content and crystallization state of the support. The catalytic activity of Pd/α-Si_3N_4 is also strongly affected by the preparation procedure. The Pd/α-Si_3N_4 catalyst obtained by aqueous impregnation is less active and less stable. It was proposed that if water is used as an impregnation solvent, the surface acid-based properties of Si_3N_4 support and/or of the Pd active phase are irreversibly damaged. Pd supported on α-Si_3N_4, prepared by impregnation of the Pd precursors in toluene solutions are found to be the most active and stable under reaction conditions.

Keywords: Catalytic combustion of methane; Silicon nitride; Palladium

1. Introduction

High temperature catalytic reactions require the use of thermostable catalysts in order to avoid a decrease of their catalytic performances with time. Usually, the materials used as supports of the active metallic phases are oxides, such as silica, alumina, silica–alumina, hexaluminates, ... These materials have rather low thermal conductivity and do not hinder sintering of the metal particles as well as of the support particles, which induces a decrease of the catalyst performances. The sintering is favoured by the presence of ''hot-spots'' in such materials. The use of highly stable materials rather chemically inert and with high thermal conductivity may be a solution to address this problem. Among refractory ceramics, silicon nitride presents very good characteristics (low density: 3.2 g/cm^3; low dilation coefficient: 3.1×10^{-6} K^{-1}; high melting/decomposition temperature: ∼2800 °C; rather chemically inert) with, above all, a rather high thermal conductivity even at high temperature (∼46 W m^{-1} K^{-1} at 1000 °C) as compared to oxides, such as silica (1 W m^{-1} K^{-1}) and alumina (9 W m^{-1} K^{-1}).

Despite its very good properties, silicon nitride was not tested as a catalyst support until recently: Pd/α-Si_3N_4 for the combustion of methane [1]. We have performed several studies that have shown the importance of several parameters on the activity and stability of these catalysts namely their synthesis conditions, the crystalline phase of silicon nitride and the presence of amorphous phase. In the following, we report the results illustrating these points.

2. Experimental

2.1. Silicon nitride powders (Table 1)

Silicon nitride has two thermodynamically stable phases both having hexagonal structure: the low temperature (<1200 °C) α-phase and the high temperature (>1500 °C) β-phase (recently a cubic γ-phase has been synthesized at high pressure). Between 1200 and 1500 °C both phases coexist. The

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Table 1
Characteristics of the silicon nitride powders

	Material			
	α-Si_3N_4	β-Si_3N_4	SiN-am	SiN-annl
Surface area (m^2/g)-BET	6	2	66	28
Structure/phases-XRD	85% α, 15% β	86% β, 13% α, 1% Si	Amorphous (>80%), $\alpha/\beta \approx 2.3$	Amorphous (<20%), $\alpha/\beta \approx 6.6$

unit cell dimension along the *c*-axis for α-phase is approximately twice the one of the β-phase.

In this work, we used different silicon nitride powders: two crystalline powders (α-Si_3N_4 from Goodfellow and β-Si_3N_4 from Johnson Matthey) and an amorphous powder (SiN-am from Johnson Matthey). The first two have relatively low surface areas 7 m^2/g for α-Si_3N_4 and 2 m^2/g for β-Si_3N_4. The latter has a measured (by BET method) surface area of 66 m^2/g and contains very few grains of crystalline silicon nitride. In order to obtain a crystalline powder with a high content of α-phase and with higher surface area than the commercially available one we carried out crystallization of the SiN-am at high temperature under N_2 flux following a procedure described elsewhere [2,3]. We obtained a new powder (SiN-annl), with a surface area of 28 m^2/g, which is mainly crystalline. Furthermore, each of the crystalline samples contains a small amount of the other phase, i.e. α-Si_3N_4 powder contains about 15% of β-Si_3N_4 and β-Si_3N_4 powder contains around 13% of α-Si_3N_4. SiN-annl contains less than 20% of amorphous material and the ratio between the crystalline phases is $\alpha/\beta \approx 6.6$.

2.2. Preparation of the catalysts

For the study on the influence of the support nature on the catalytic performances of the catalysts, the catalysts were prepared by impregnation of the different supports (α-Si_3N_4, β-Si_3N_4, SiN-am and SiN-annl) with adequate amounts of Pd(II)-bis-acetylacetonate [$Pd(C_5H_7O_2)_2$] dissolved in toluene. For the study on the influence of the solvent used in the preparation method on the catalytic performances of the catalysts, these were prepared by impregnation of α-Si_3N_4 with adequate amounts of Pd(II)-acetate [$Pd(CH_3CO_2)_2$] dissolved either in toluene or in water. In both cases, we used an excess of solvent. After impregnation, evaporation of the solvent and drying, the catalysts precursors were decomposed under argon flow at 500 °C for 2 h. They were then calcined during 2 h at 350 °C under oxygen flow and further reduced under hydrogen flow at 500 °C (in both cases the heating rate was 1 K min^{-1}). The content of Pd is always ∼0.5% in weight.

2.3. Techniques used to characterize the supports and the catalysts

2.3.1. X-ray diffraction

Phase composition and crystalline state of the silicon nitride supports was controlled by X-ray diffraction using a Bruker D5005 powder diffractometer where the sample is fixed and the X-ray tube (Cu Kα1 + α2; λ = 0.154184 nm) and the detector rotate. Each spectrum is acquired in a 2θ range from 3° to 80° using 0.020° steps and acquisition time of 16 s/step. The method of quantification of the ratio of crystalline phases is described elsewhere [2].

2.3.2. X-ray photoelectron spectroscopy and low energy ion scattering spectroscopy

The chemical state of the surface of the silicon nitride supports and of the supported Pd catalysts was checked by XPS. The XPS spectra were obtained on an ESCALAB 200R spectrometer (FISONS Instruments) using the Mg Kα line (1253.6 eV) as an excitation source. The pass energy of the hemispherical electron analyzer was 50 eV, and the angle of the photoelectrons with respect to the plane of the surface was 90°. All data are corrected taking as a reference the N 1s level of Si_3N_4 (397.6 eV). Quantitative analysis of the XPS data was carried out using the software attached to the apparatus, taking into account the atomic sensitivity factors, the transmission of the analyzer and the photoelectrons mean paths in the material.

Low energy ion scattering spectroscopy (LEIS) allows the analysis of the surface chemical composition by sputtering atomic layer by atomic layer the surface of the material. The experiments were performed in the same equipment as the XPS analysis. We used $^4He^+$ ions with a primary energy of 1 keV and an intensity of 50 nA over a surface of ∼0.1 mm^2.

2.3.3. Transmission electron microscopy

The morphology and structure of the silicon nitride supports and Pd catalysts were studied by transmission electron microscopy (TEM). The microscope is a JEOL JEM 2010, operated at 200 kV, equipped with a LaB_6 tip, a high resolution pole-piece and a Pentafet-LinK ISIS energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments). The samples were dispersed in ethanol. A drop of this suspension was disposed on a holey-carbon thin film supported on a microscopy copper grid (3.05 mm, 200 mesh). The palladium particle size was determined from the size histograms (performed over more than 400 particles) measured from TEM images. Further EDX analysis over nanometer size regions were performed on a similar microscope equipped with a field emission gun capable of yielding sub-nanometer electron probes with sufficient intensity.

2.3.4. BET

Specific BET surface areas of the supports were determined by argon adsorption using an home made automatic adsorption apparatus.

2.3.5. Chemical analysis

Induced coupled plasma (ICP) chemical analysis was used to determine the metal contents. The palladium from the samples was dissolved in a mixture H_2SO_4/HNO_3/HF at 250 °C and HF + (2/3) HCl/(1/3) HNO_3 at 150–200 °C. The acidic treatment did not dissolve completely the silicon nitride support and a white-grey residue was observed. The solutions were filtered before analysis by optical ICP in a SPECTRO monochromatic spectrophotometer (Pd wavelength −340.6 nm).

2.3.6. TPD of oxygen

The temperature programmed desorption (TPD) experiments were performed in the flow system and the desorption of the gases was analyzed by mass-spectrometry. Prior to the measurements, the samples (0.9 g), fixed in a quartz reactor, were treated in a helium flow (100 ml/min, for 6 h) at temperatures ranging from 25 to 800 °C and than treated with oxygen at 800 °C for 1 h. The TPD spectra of oxygen were recorded in a helium flow (100 ml/min) under the conditions of a linearly increasing temperature (5 °C/min).

2.4. Catalytic tests

Total oxidation of methane was performed between 25 and 650 °C in a flow tubular quartz reactor with a stationary layer of catalyst. The temperature of the catalysts was measured using a thermocouple with its end in the catalytic bed. The catalytic bed was nearby 2 mm and located in the middle of the furnace (30 cm length). A 0.2 g mass loading of catalyst was used for each experiment. The flow of reactants (methane, oxygen and nitrogen in ratio 2.5/19.5/78) was maintained at 100 ml/min. The products were analyzed by mass-spectrometry. CO_2 and H_2O were the only products. Methane conversion versus temperature was measured for the fresh catalysts and after a first reaction cycle including 3 h at 650 °C.

3. Results and discussion

The characteristics of the catalysts are reported in Table 2. We can note that the mean size of the Pd particles decreases with increasing specific surface area of the supports. For the amorphous support, the binding energy of Pd (335.3 eV) is similar to that of bulk Pd [1] indicating that no particular interaction between the Pd particles and the support exists; on the contrary, on the crystalline supports the binding energy of Pd is rather high indicating a modification of the electronic properties of the Pd particles through a specific interaction.

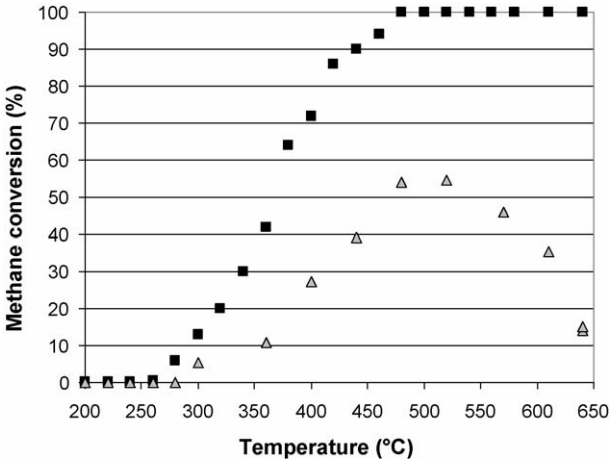

Fig. 1. Conversion of methane for both samples in the reaction of total oxidation of methane (CH_4 (2.5%), O_2 (19.5%), N_2 (78%); 100 ml/min) as a function of temperature for the fresh catalysts showing a deactivation during reaction for Pd/β-Si_3N_4 (triangles) compared to Pd/α-Si_3N_4 (squares).

3.1. Influence of the nature of the support

3.1.1. Comparison of Pd/α-Si_3N_4 and Pd/β-Si_3N_4

The catalytic activity of Pd fresh catalysts supported on both crystalline phases of silicon nitride is reported in Fig. 1, where we can see that Pd/α-Si_3N_4 is very active and behaves as in previous works [1] with a half-conversion temperature (T_{50}) around 350 °C and achieving total conversion before 400 °C. On the contrary, Pd/β-Si_3N_4 deactivates during reaction. Indeed, from the early stages of reaction we can note a shift towards higher temperatures for equal conversion as compared to Pd/α-Si_3N_4, revealing a less active catalyst. This shift increases at higher temperatures and a decrease in conversion is observed above 500 °C. After a first cycle of reaction and 3 h at 650 °C under reaction conditions, Pd/α-Si_3N_4 remains stable and active [1,4] while Pd/β-Si_3N_4 has only a very low (<10%) residual activity [4].

This difference in behaviour cannot be explained by the almost inexistent differences in the characteristics of the catalysts after reaction (Table 3). Indeed, the sintering is rather limited for both catalysts as expected. It is even inexistent for the catalyst that deactivates (Pd/β-Si_3N_4). The Pd binding energy reveals that the particles are oxidized [5] after reaction as it is normal for such conditions of temperature and partial pressure of oxygen.

The analysis of the TEM images obtained at higher resolution reveals, however, a fundamental difference. Many

Table 2
Characteristics of the fresh catalysts

	Influence of the nature of the support (Pd-bis-acetylacetonate in toluene)				Influence of the solvent (Pd/α-Si_3N_4 with Pd-acetate)	
	α-Si_3N_4[a]	β-Si_3N_4[a]	SiN-am[a]	SiN-annl[a]	In toluene	In water
Mean diameter (nm)-TEM	4.3	5.6	2.9	3.2	4.9	5.0
Pd-3$d_{5/2}$BE (eV)-XPS	335.9	335.8	335.3	335.9	335.6	335.8

[a] Catalyst.

Table 3
Characteristics of the catalysts supported on different silicon nitride powders after reaction

	Catalyst			
	α-Si_3N_4	β-Si_3N_4	SiN-am	SiN-annl
Mean diameter (nm)-TEM	5.8	5.7	3.2	3.6
Pd-$3d_{5/2}$ BE (eV)-XPS	337.3	337.0	337.1	337.3

of the Pd particles in the Pd/β-Si_3N_4 catalyst after reaction are coated by a sub-nanometer amorphous layer (Fig. 2), which is not the case for the Pd/α-Si_3N_4 catalyst (Fig. 3). Local analysis by EDX with sub-nanometer electron probes indicates that this layer is SiO_x. Some particles are only partially coated (Fig. 2c).

TEM gives a view at a local level. In order to be sure that the coating of the particles is characteristic of the whole sample, we performed analysis with a more global technique, which is sensitive to surface. This is the case of LEIS where a layer by layer sputtering over 0.1 mm^2 areas with energetic ions ($^4He^+$, 1 keV) allows chemical analysis of the surface and so yields depth composition profiles. The results reported in Fig. 4 clearly show that for Pd/α-Si_3N_4 the Pd signal is readily detected for the first spectrum acquired at the beginning of sputtering. The intensity of the Pd peaks does not change significantly as the sputtering continues. On the contrary, the Pd peak detected for Pd/β-Si_3N_4 is very weak at the beginning of the analysis and continuously increases as the sputtering proceeds revealing the presence of a layer on the surface of the Pd particles.

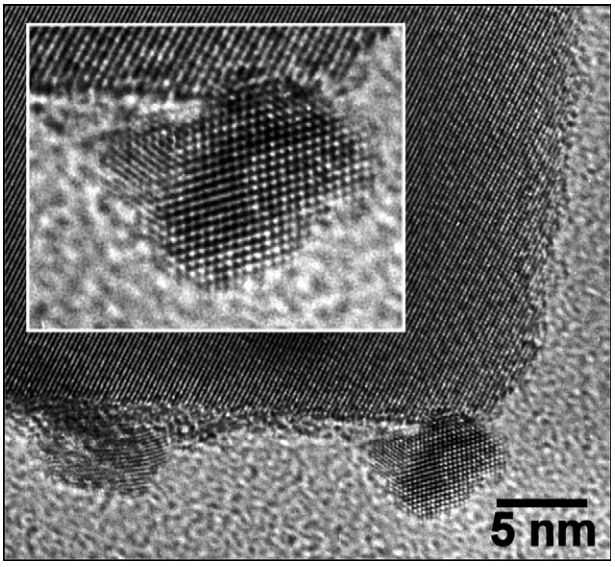

Fig. 3. TEM image of Pd/α-Si_3N_4 catalyst after reaction. Insert: PdO particle oriented in the [−1 1 −1] direction.

The coating is certainly a continuous process that begins in the first stages of the reaction and becomes more pronounced at higher temperatures. This can explain why the Pd particles do not sinter at all for Pd/β-Si_3N_4. It is known that β-phase-rich silicon nitrides are more sensitive to oxidation than α-phase-rich silicon nitrides at very high temperatures (above 1000 °C) [6] due to its channel-structure allowing diffusion of oxygen in the lattice. We can therefore

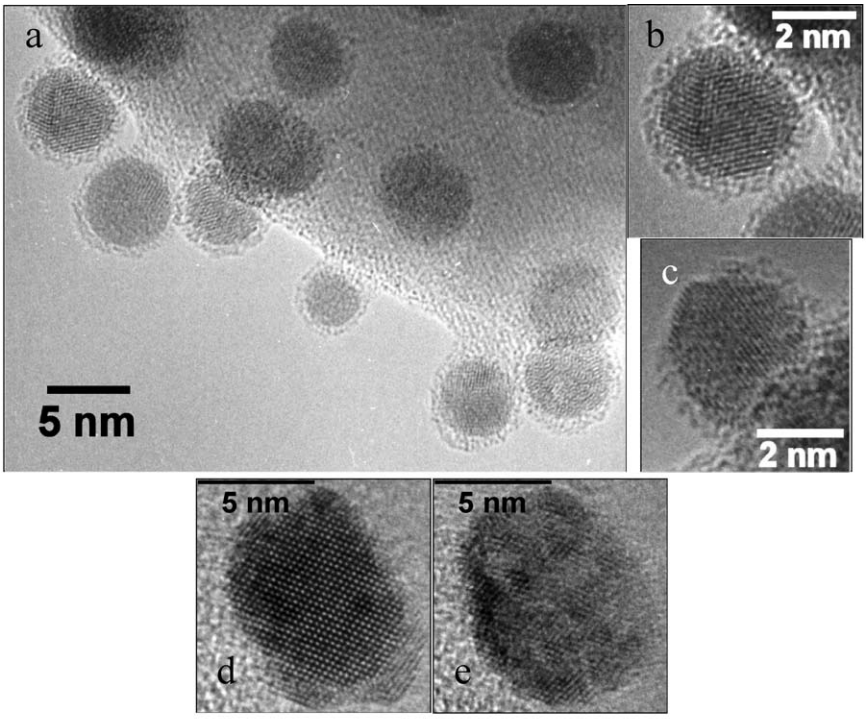

Fig. 2. TEM images of Pd/β-Si_3N_4 catalyst after reaction. (a) General view with several coated particles. Detail of a completely (b) and a partially (c) coated particle. (d and e) High resolution images at different defocusing conditions: (d) focused image revealing the PdO lattice oriented in the [−1 1 −1] direction; (e) under-focused image of the same particle revealing the amorphous layer over the particle.

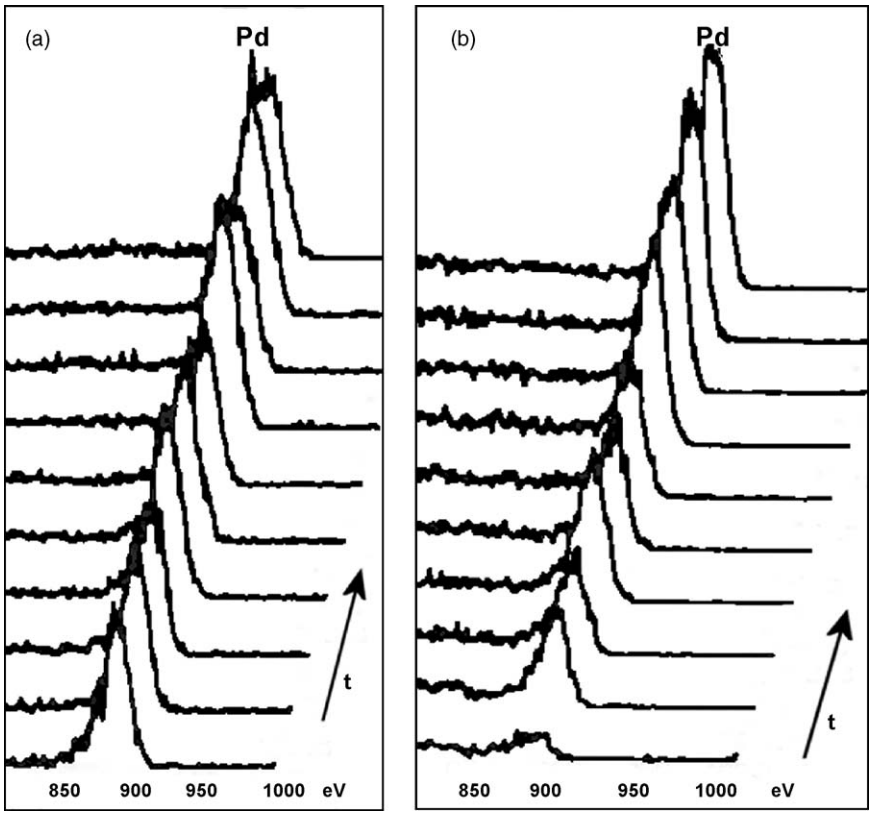

Fig. 4. LEIS spectra of samples after reaction: (a) Pd/α-Si_3N_4 and (b) Pd/β-Si_3N_4.

suppose that the coating process of the particles that we observe is due to the same phenomenon that begins, at lower temperatures, on the surface before extending, at higher temperatures, to the bulk [6,7]. Indeed, destructuring of sub-nanometer layers of the surface may allow diffusion of silicon to the surface of the Pd particles, which is subsequently oxidized leading to the formation of the amorphous SiO_x coating. The use of α-Si_3N_4 is thus essential for good catalytic performances.

3.1.2. Role of the amorphous fraction

Smaller Pd particles, and thus a better dispersed catalyst, can be obtained if we increase the surface area of the support. We were able to achieve this by using amorphous silicon nitride (SiN-am) with 66 m^2/g (Table 2). High temperature crystallization of this support under nitrogen yields a high content α-phase powder with 28 m^2/g surface area (SiN-annl), which is much higher than the commercially available α-Si_3N_4 (6 m^2/g).

The performances of Pd/SiN-am and Pd/SiN-annl fresh catalysts in the combustion of methane (Fig. 5) show half-conversion temperatures of 430 and 370 °C, respectively, which are higher than for Pd/α-Si_3N_4 (350 °C). Furthermore, after a cycle of reaction and 3 h at 650 °C under reaction conditions, both catalyst show even lower activity (Fig. 5). The decrease in activity is stronger for Pd/SiN-am (total conversion is not attained) than for Pd/SiN-annl. The activity increases with increasing content of α-Si_3N_4 and decreasing content of amorphous silicon nitride. General characteristics of the

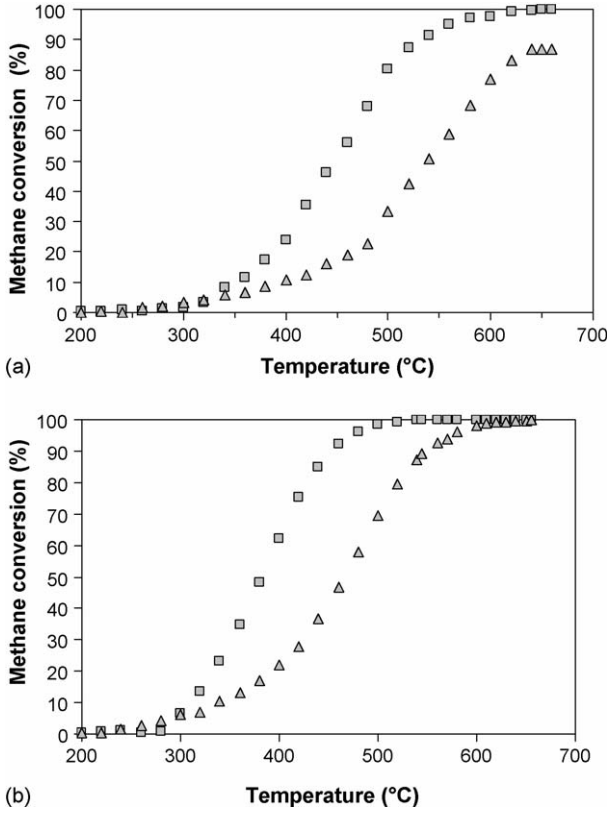

Fig. 5. Conversion of methane in the reaction of total oxidation of methane (CH_4 (2.5%), O_2 (19.5%), N_2 (78%); 100 ml/min) as a function of temperature for the fresh catalyst (squares) and the catalyst having worked for 3 h at 650 °C in reaction conditions (triangles): (a) Pd/SiN-am and (b) Pd/SiN-annl.

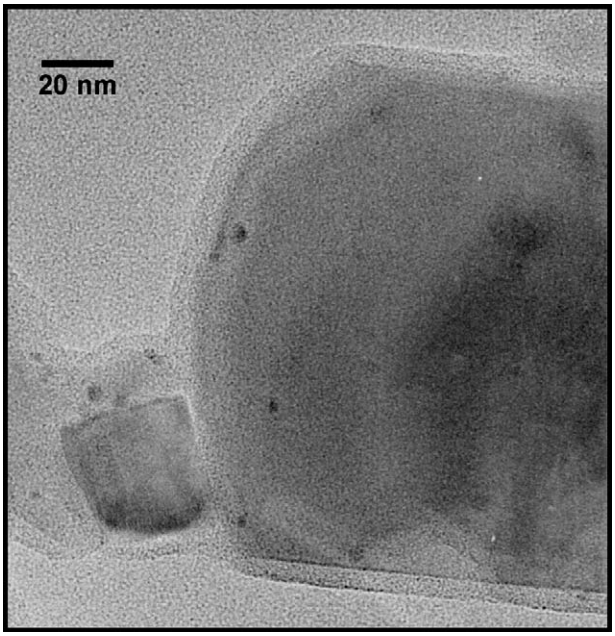

Fig. 6. TEM image of the Pd/SiN-annl after reaction showing the coating of the catalyst by an amorphous phase.

catalysts after reaction (Table 3) show that the sintering is very limited. However, from the XPS Si-2p signal one can see that the amount of SiO_2 formed on Pd/SiN-am is higher than that formed on Pd/SiN-annl [2]. TEM images show also that an amorphous layer coats the Pd particle as well as the crystalline grains of the support, in many regions of the sample (Fig. 6). The amorphous fraction of the support must be mobile at high temperatures at which it oxidizes to form a coating over the catalyst.

3.1.3. General comparison

Pd catalysts supported on both β-Si_3N_4 and silicon nitride powders containing non-negligible amounts of amorphous phase (SiN-am and SiN-annl) showed poor performances in the total oxidation of methane compared to those supported on α-Si_3N_4. The deactivation on those catalysts is due to a coating, with an amorphous SiO_x layer, of the active phase for Pd/β-Si_3N_4 and of the active phase and the crystalline grains of the support for Pd/SiN-am and Pd/SiN-annl. The process of formation of the amorphous coating is certainly different in the two cases. Indeed, for Pd/β-Si_3N_4 it could be related to the low resistance of the β-Si_3N_4 to oxidation at high temperatures; for Pd/SiN-am and Pd/SiN-annl it could be due to diffusion and oxidation of mobile amorphous species at high temperatures.

3.2. Influence of solvent used in the preparation method

Preparation in organic compounds is certainly a drawback for industrial transfer of our approach. We have thus tried to develop preparation procedures in water. Since Pd-bis-acetylacetonate is not soluble in water, we opted for using Pd-acetate, which is both soluble in water and toluene. We, then, compared the performances in the combustion of methane for catalyst prepared

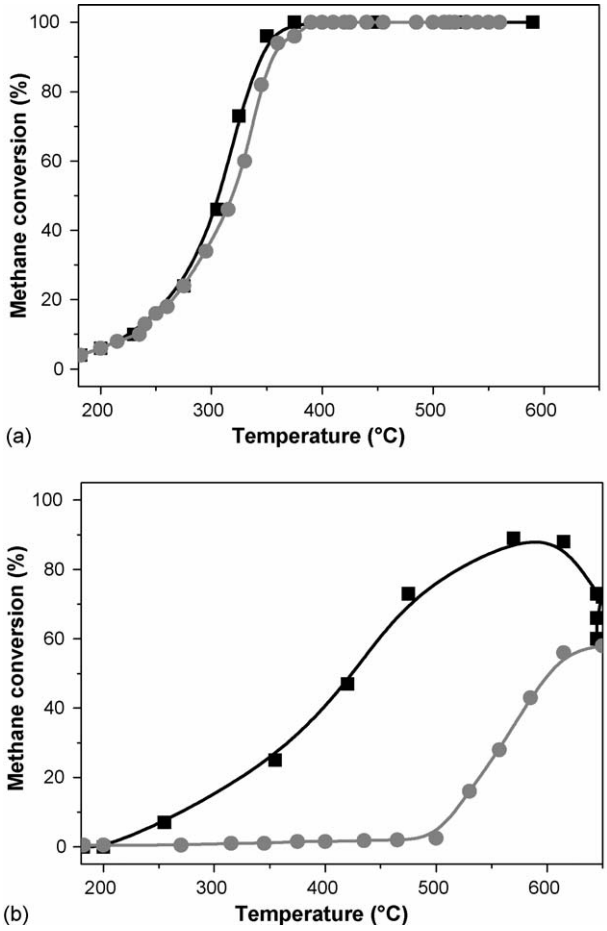

Fig. 7. Conversion of methane in the reaction of total oxidation of methane (CH_4 (2.5%), O_2 (19.5%), N_2 (78%); 100 ml/min) as a function of temperature for the fresh catalysts (black squares and line) and the catalysts having worked for 3 h at 650 °C in reaction conditions (grey circles and line) showing a deactivation of the catalyst prepared in water (b) compared to the one prepared in toluene (a).

by impregnation of α-Si_3N_4 with Pd-acetate in toluene (Pd/α-Si_3N_4-tol) and water (Pd/α-Si_3N_4-wat) solutions.

The catalyst prepared in toluene was the most effective. The total conversion of methane in the experimental conditions was achieved already at 400 °C (Fig. 7a) and the half-conversion temperature is similar to that of Pd/α-Si_3N_4 prepared with Pd-bis-acetylacetonate in toluene. The catalyst remains active and stable after 3 h at 650 °C under reaction conditions (Fig. 7a). Conversely, the Pd/α-Si_3N_4 catalyst obtained by aqueous impregnation is less active and less stable.

Total conversion of methane was never attained and the catalysts deactivates during the first cycle of reaction (Fig. 7b). The catalytic behavior is very different despite initial similar average size (Table 2) and dispersion of the active phase

Table 4
Characteristics of the catalysts prepared in water and toluene after reaction

	Catalyst in toluene	Catalyst in water
Mean diameter (nm)-TEM	6.0	8.3
Pd-$3d_{5/2}$ BE (eV)-XPS	337.4	337.3

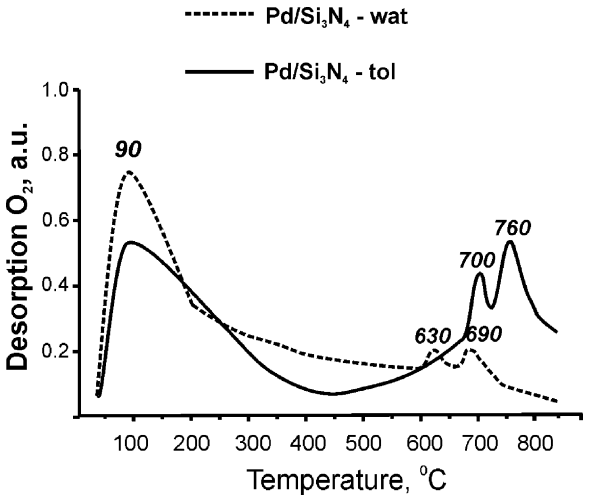

Fig. 8. TPD of oxygen for Pd/α-Si_3N_4-tol (bold line) and for Pd/α-Si_3N_4-wat (dotted line) obtained after interaction of the samples with O_2 at 800 °C for 1 h.

observed by TEM for both catalysts. The sintering of Pd particles during reaction is stronger for the catalyst prepared in water (Table 4). However, the increase in size (around the double) and the consequent decrease of available active sites cannot explain such a strong deactivation [8,9]. Furthermore, no coating is observed by TEM.

To evaluate the relations between the catalytic activity and the redox properties of the catalysts, TPD of oxygen experiments were carried out. For both samples, we obtain a low-temperature desorption peak around 90 °C and two high-temperature desorption peaks around 700 °C (Fig. 8). The former can be attributed to weakly bound oxygen species on Pd and support while the latter generally attributed to stabilized oxide species (PdO_x). But the TPD profiles of oxygen from Pd significantly changed depending on the preparation.

We observed that the weakly bound species desorb over a larger range of temperatures for Pd/α-Si_3N_4-tol than for Pd/α-Si_3N_4-wat. The area under this low-temperature peak is also larger for Pd/α-Si_3N_4-tol revealing a larger amount of weakly bound species for this catalyst. High-temperature desorption peaks are shifted to higher temperatures for Pd/α-Si_3N_4-tol (700 and 760 °C, instead of 630 and 690 °C for Pd/α-Si_3N_4-wat). For this active catalyst, a strong interaction between Pd and oxygen is thus evidenced. This strong interaction may induce the presence of reactive oxygen (weakly bound species) at the surface of the active phase [10]. We can suppose that if water is used as an impregnation solvent, the surface acid-based properties of Si_3N_4 support and/or of the Pd active phase may be irreversibly damaged.

The catalytic activity of Pd/α-Si_3N_4 is strongly affected by the preparation procedure.

4. Conclusion

These studies have clearly shown that Pd/α-Si_3N_4 (prepared by impregnation in toluene) is an outstanding catalyst for high temperature reactions, such as the combustion of methane. We have also evidenced that the use of β-Si_3N_4, the presence of large amounts of amorphous silicon nitride as well as impregnation in aqueous solutions are noxious for the catalytic performances.

Despite the poor performances of the catalysts prepared in aqueous solutions, we have already shown that silicon nitride used as support of catalysts is suitable for industrial applications since radiant panels based on an α-Si_3N_4 supported Pd catalyst (used for infrared emission obtained from catalytic combustion of natural gas, in order to thermoforming plastics, dry paints, ...) were successfully tested for more than 2500 h at temperatures around 1000 °C [11].

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