



METHANE COMBUSTION OVER Pd/CexZr1-xO2/SiO2 CATALYSTS: EFFECTS OF PALLADIUM INTRODUCTION STEP

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Abstract

CexZr1-xO2/SiO2 (CeZr-O2/SiO2) mixed oxides were synthesized using sol-gel process and supercritical drying methods. Pd/CexZr1-xO2/SiO2 catalysts have been evaluated in methane combustion in an attempt to investigate the effects of the preparation method and the different addition step of palladium precursor on the oxidation activity of supported Pd catalysts for this greenhouse gas. The metal was deposited by impregnation of palladium acetate (Pd(OAc)2) on dried or calcined CeZr-O2/SiO2 support or in situ by sol-gel process during the preparation of the support. The properties of the as-synthesized catalysts, such as textural structure, surface chemical state, surface acidity and the oxygen storage capacity (OSC) were determined using N2-physical adsorption/desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of NH3 (TPD-NH3) and O2 (TPD-O2) in order to correlate their activity with their physicochemical properties.

Among all the catalysts tested the sample prepared by impregnation (on dried or calcined CeZr-O2/SiO2 support) presented the higher activity for methane combustion. These results could be due to the good dispersion and stability of PdO species on CeZr-O2/SiO2 surface, the large surface area, the weak acidity and the higher OSC compared to the catalyst prepared by sol-gel process.

Key Words: Sol-gel process, CeZr-O2/SiO2, Pd/CexZr1-xO2/SiO2 catalysts, Methane combustion.

1. Introduction

For applications in gas turbines and boilers, there is an urgent need for the development of thermo-stable catalysts for natural gas combustion. Many efforts have been performed to design new catalytic materials that exhibit good performances [1]. These catalysts should be able to oxidize completely exhaust methane at low temperatures and avoid the NO_x emissions. Supported palladium has been reported to be the most effective catalyst for methane combustion [2,3]. Palladium dispersion and palladium-support interaction play important roles in the catalytic performance [4], that's why a wise choice of support must be taken [5]. The most widely used support is Al₂O₃. However, palladium catalysts supported by alumina are not stable due to γ -alumina easily occurs at high temperatures [6]. The use of SiO₂ as a support could promote OSC due to the relatively high surface area, its dispersive properties and the relatively inert character compared to other supports [7]. Several studies tried to improve the performance of Pd catalysts with the use of promoters. Among the effective promoters, cerium oxide was suggested as a promising candidate, due to its stability improvement toward coke formation [8]. This capability is related to the high oxygen storage capacity, the high oxygen mobility and the cerium ability to switch easily between the oxidized and reduced states. All these properties are often associated to the presence of oxygen vacancies [9,10]. Moreover, the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the ceria lattice leads to enhance cerium redox properties, thermal resistance, and catalytic behaviour [11,12]. From these results, the solid Pd / CeO₂-ZrO₂ / SiO₂ seems to be a good choice for using in the catalytic methane combustion. All we need now is to choose an adequate method to synthesize it. In fact, the nature of the metal-support interaction may strongly influence the catalyst thermal stability and activity. So the method used should conserve the advantages of Ce-Zr-O, silica and palladium. To synthesize this complex (Ce-Zr-O) various methods have been reported in the literature.

For instance, Zhao et al.[13] used the sol-gel methods combined with supercritical drying techniques to prepare Ce-Zr/Al₂O₃ mixed oxide. Zhou et al.[14] prepare Ce-Zr/Al₂O₃ support by co-impregnation and Pd/Ce-Zr/Al₂O₃ catalysts are prepared by impregnation method. Supandi et al. [15], prepare the Pt/CeO₂-ZrO₂-SnO₂/SBA-16 catalyst by using co-precipitation and impregnation methods. Iryna et al. [16] synthesize CeO₂-ZrO₂/SiO₂ nanocomposite oxides by a liquid-phase method.

Several studies focus on this complex and they studies many effects such as ceria-zirconia ration, amount... Nevertheless, there are no frequent investigations about palladium introduction step into CeZr/SiO₂ support for the catalytic methane combustion.

In this work, the sol-gel process was used to prepare the SiO₂ aerogel due to its relative high surface area. The addition step of palladium precursor is changed in order to modify the Pd-support interaction and yet to study its effects on the catalytic activity in methane combustion.

2. EXPERIMENTAL

2.1 Chemicals

Cerium nitrate Ce(NO₃)₃.6H₂O (Sigma-Aldrich, 99.99%), zirconium(IV) oxynitrate hydrate ZrO(NO₃)₃.xH₂O (Sigma-Aldrich, 99.99%), ethanol C₂H₅OH (Sigma-Aldrich, \geq 99.8%), tetraethyl orthosilicate Si(OC₂H₅)₄ (TEOS) (ACROS, 98%), acetic acid CH₃COOH (Sigma-

Aldrich, $\geq 99.7\%$) and palladium acetate ($\text{Pd}(\text{OAc})_2$) (Sigma-Aldrich, 98%) are used as chemicals in this work.

2.1 Support preparation

The $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{SiO}_2$ supports were synthesized using a sol-gel process. A mixture of hexahydrated cerium (III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Zirconium(IV) oxynitrate hydrate ($\text{ZrO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), acetic acid (CH_3COOH), tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS)), were dissolved in ethanol $\text{C}_2\text{H}_5\text{OH}$ and deionized water at 40°C . The molar ratios of $\text{H}_2\text{O}/\text{TEOS} = 15$, $\text{CH}_3\text{COOH}/\text{TEOS} = 1$ and $\text{Ce}/\text{Zr} = 1/2$. The Zr loading on silica is equal to 15 wt%. The sol is maintained under constant stirring until a spongy and transparent gel is gained. The produced gel was aged for 24 h at 8°C , the solvent is removed by evaporation under supercritical conditions of ethanol ($T_c = 240.9^\circ\text{C}$, $P_c = 6.14 \text{ MPa}$). Finally, the obtained solid is calcined at 550°C for 4 h with a temperature ramp of $2^\circ\text{C}/\text{min}$ up to 550°C under oxygen flow (30 ml/min).

2.2 Catalysts preparation

The $\text{Pd}_z/\text{CeZr-O}_2/\text{SiO}_2$ catalysts were prepared with different palladium addition steps using palladium acetate $\text{Pd}(\text{OAc})_2$ as a precursor and with a designed metal loading of 0.5 wt%. z represents the method of incorporation of $\text{Pd}(\text{OAc})_2$: $z = \text{insitu}$, d or c . Indeed, three catalysts were synthesized: $\text{Pd}_{\text{insitu}}/\text{CeZr-O}_2/\text{SiO}_2$ catalyst is prepared by adding the $\text{Pd}(\text{OAc})_2$ in the sol-gel solution during the $\text{CeZr-O}_2/\text{SiO}_2$ preparation. $\text{Pd}_d/\text{CeZr-O}_2/\text{SiO}_2$ and $\text{Pd}_c/\text{CeZr-O}_2/\text{SiO}_2$ catalysts were prepared respectively, by impregnation on dried or calcined support. In fact, appropriate amounts of $\text{Pd}(\text{OAc})_2$ and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{SiO}_2$ support (dried or calcined) are ground in an agate mortar for 10 min. Then, acetone is added until obtaining a paste which is dried at 60°C . The obtained catalysts were calcined in flowing oxygen (30 mL/min) at 550°C for 4 h

2.3 Catalyst characterization

BET surface area is determined from N_2 adsorption/desorption isotherms at 77K measurements using an automatic Micrometrics ASAP 2000 Analyzer. The samples were degassed for 4 h at 200°C under vacuum. The pore size distributions were determined by the BJH method, using the desorption branches of isotherms. The total pore volume was estimated by means of the total amount of adsorbed gas at relative pressure $P/P_0 = 0.98$.

Palladium dispersion was determined by the dynamic pulsed hydrogen chemisorption technique. Prior to the measurements, 50 mg of sample was reduced in H_2 flow (20 mL/min) at 300°C , evacuated under nitrogen at 320°C and then cooled to room temperature. The H_2 chemisorption was carried out using a Thermal Conductivity Detector (TCD).

Acidity of the supports was determined by using NH_3 -TPD technique. The temperature-programmed desorption (TPD) measurement were performed on a Micromeritics TPD/TPR 2900 instrument. 50 mg of sample is fixed in the middle of a quartz tubular reactor by packing with

quartz wool at both ends. A mass spectrometer was used for continuous monitoring of the desorbed ammonia and the areas under the peaks were integrated. Prior to TPD measurements, samples were pretreated at 100°C for 30 min in a flow of helium gas (20 mL min⁻¹) then cooled at 50°C. Samples were then saturated with 2.5% ultrapure anhydrous ammonia gas (balance He, 20 mL min⁻¹) for 30 min and subsequently flushed with He (20 mL min⁻¹) at 50°C for 30 min to remove the physisorbed ammonia. The heating rate for the TPD measurements, from 50 to 600°C, was 10°C min⁻¹.

The oxygen storage capacity (OSC) of the catalysts was determined by O₂-TPD technique. The same steps of NH₃-TPD are performed, only ammonia is switched by 2 % O₂/He mixture.

XPS experiments were carried out on a SPECS-PHOIBOS system equipped with a hemispherical electron analyser operating in a constant pass energy, using Mg Ka radiation (hν = 1253.6 eV). The samples (0.2 mg) were fixed to the sample holder using a carbon adhesive tape and analyzed without further treatments. Spectra were analyzed with CasaXPS software and RSP database by fitting after Shirley background correction.

The crystal structure of the catalyst samples was determined by X-ray diffraction (XRD) using a D8 ADVANCE Bruker apparatus operated at monochromatic Cu Kα radiation (30 mA and 40 kV). XRD patterns are recorded in the 2θ range of 10–60°.

Catalytic activity for methane combustion is determined over the calcined sample in a dynamic micro-reactor. 0.1 g of the catalyst is used. The gas feed mixture (1 vol% CH₄, 4 vol% O₂ in He) and was flown at a rate of 100 ml/min. The reactor effluent was analyzed on line using a gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak column. The light-off experiments were performed by decreasing the temperature of the catalytic bed from 500°C by steps of 25°C (standing for 30 min at each step). The methane conversion and the turnover frequencies (TOF) were calculated by the following equations:

$$\text{Conversion (\%)} = \frac{P_{CO_2}}{P_{CH_4} + P_{CO_2}} \times 100$$

P_{CH₄} and P_{CO₂} are respectively, the partial pressures of methane and carbon dioxide.

$$\text{TOF} = \frac{A \times M_{Pd}}{l \times D}$$

$$A = \frac{P_{CO_2} \times D_T \times 273}{22.4 \times T_r \times m}$$

A: catalyst activity (%), M_{Pd}: atomic mass of palladium (106.42 g/mol), l: Pd loading (wt %), D_T: total gas flow (L/h), T_r: room temperature, m: catalyst weight (g) and D the dispersion (%).

3. Results and discussion

3.1. Nitrogen physisorption

Fig.1 shows the N₂-adsorption-desorption isotherms of Pd_z/CeZr-O₂/SiO₂ catalysts. According to IUPAC classification, all the isotherms are of type IV and with a well-defined hysteresis loop of type H1, which is typically observed for materials with mesoporous structure and uniform cylindrical pores. The steep increases of the adsorption volume at P/P₀ (0.6–0.9) are due to capillary condensation of nitrogen in the mesopores. **Table 1** compiles the BET surface area and the pore properties of all prepared catalysts. As can be noted, the textural properties of palladium catalysts depend significantly on the order of palladium addition. Consequently, the BET surface area (*S*_{BET}) varies between 600 and 795 m²/g and the pore volume (*V*_p) varies between 0.95 and 2.00 cm³/g. Besides, the catalyst prepared by incorporation of palladium on the dried CeZr-O₂/SiO₂ support, referred to as Pd_d/CeZr-O₂/SiO₂, exhibit the highest surface area (796 m²/g) and a pore volume of 2.00 cm³/g that is larger than the two other catalysts prepared by the addition of palladium precursor in situ or by impregnation on calcined support. These results suggest that the impregnation of Pd(OAc)₂ on dried support is more beneficial and leads to better textural properties. Likewise, **Fig.2** shows a typical BJH pore size distribution for the studied catalysts. What can be observed is that Pd_d/CeZr-O₂/SiO₂ catalyst is more homogeneous and has a bimodale pore distribution with maxima centered at 64 and 95 Å. Nevertheless, the drop of the BET surface area of Pd_o/CeZr-O₂/SiO₂ and Pd_{insitu}/CeZr-O₂/SiO₂ samples is mainly related to the changes in the catalysts pore structure. In fact, the shift towards lower pore diameter and the drop in the total pore volume compared to Pd_d/CeZr-O₂/SiO₂ may be explained by the blockage of the pores by oxide particles. [17, 18]

Table 1

BET surface area, main pore diameter *D*_p (Å), pore volume *V*_p (cm³/g), palladium dispersion (*D*_{H₂}, %) and PdO particles size (nm) of CeZr-O₂/SiO₂ and Pd_z/CeZr-O₂/SiO₂ catalysts.

<i>Catalysts</i>	<i>S</i> _{BET} ^a m ² /g	<i>D</i> _p ^a (Å)			<i>V</i> _p ^b (cm ³ /g)	<i>D</i> _{H₂} ^c (%)	<i>PdO particles size</i> ^c (nm)
		1 st type	2 nd type	3 rd type			
CeZr-O ₂ /SiO ₂	614	27	38	48	0.83	-	-
Pd _{insitu} /CeZr-O ₂ /SiO ₂	600	38	55	90	1.00	4	29
Pd _d /CeZr-O ₂ /SiO ₂	795	-	64	95	2.00	34	3.3
Pd _o /CeZr-O ₂ /SiO ₂	680	38	48	74	0.95	25	4.5

^aFrom N₂ chemisorption at 77 K using the BET equation.

^bTotal pore volume estimated at rrelative pressure P/P₀ = 0.99, accuracy ± 0.01 cm³/g.

^cBased on H₂ chemisorption measurements.

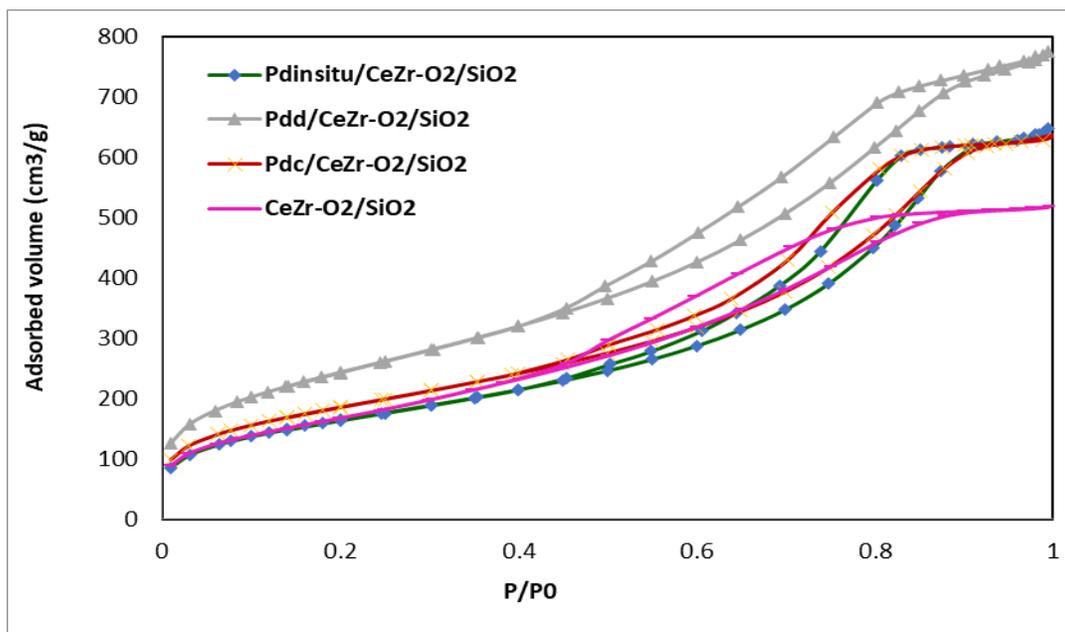


Fig.1. Adsorption-desorption isotherm profiles of CeZr-O₂/SiO₂ and Pd₂/CeZr-O₂/SiO₂ catalysts.

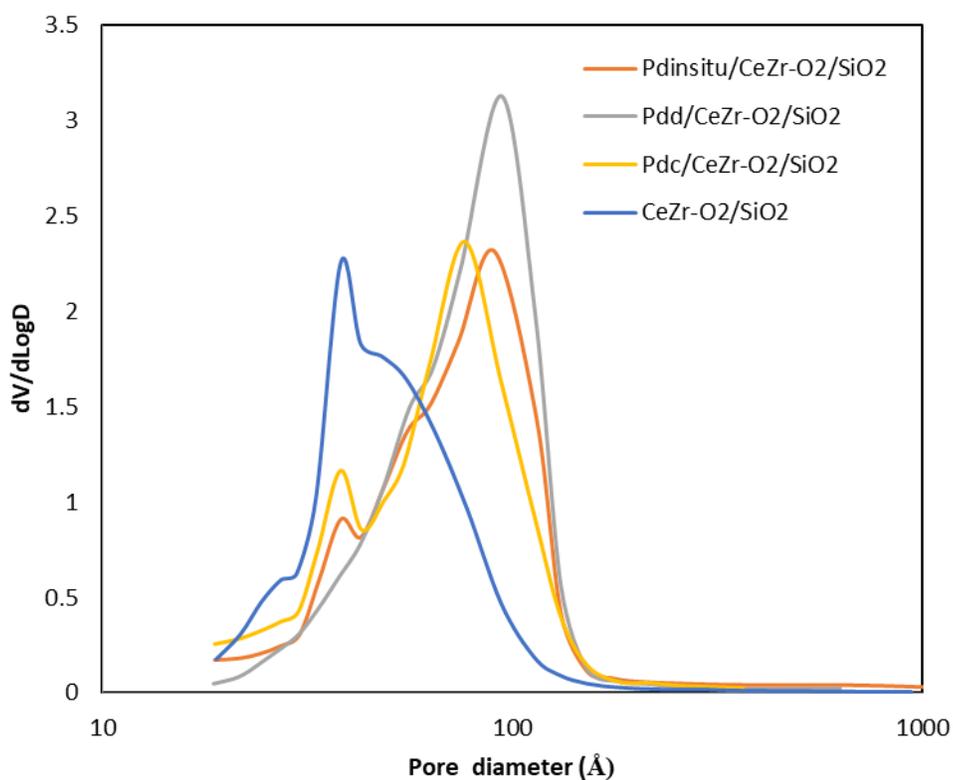


Fig.2. Average pore distributions of Pd₂/CeZr-O₂/SiO₂ catalysts.

3.2. Palladium dispersion

The dispersion and the crystallite size of palladium are accomplished by the H₂ chemisorption measurements. The obtained results compiled in **Table 1**, reflect the significant influence of the preparation procedure on the palladium dispersion of the prepared catalysts. In fact, Pd dispersion decreases in the following order: Pd_d/CeZr-O₂/SiO₂ > Pd_z/CeZr-O₂/SiO₂ > Pd_{insitu}/CeZr-O₂/SiO₂. These results suggest that the addition of palladium precursor by impregnation enhance greatly the dispersion of palladium oxide in comparison with the sol-gel method. Indeed, the low dispersion observed in the Pd_{insitu}/CeZr-O₂/SiO₂ may be explained either by the encapsulation of an important amount of palladium within the pores of support and/or by the agglomeration of oxide particles and the sintering of the active phase. Similar phenomenon has been observed in the literature [19,20]. What is worth noticing is that Pd_d/CeZr-O₂/SiO₂ catalysts show the best dispersion (34%) which may probably be related to the homogeneity of this sample. In fact, more the catalyst is homogeneous higher is the dispersion. Moreover, it has been established in the literature. that the acid/base properties of the support affect greatly the palladium dispersion. Recent work in our laboratory [19] shows that the introduction of Zr increases the acidity of alumina which contributes to a decrease in PdO dispersion that corresponds to our results. In fact, the enhancement in PdO dispersion is related to the decrease in acidity strength of Pd_d/CeZr-O₂/SiO₂ and Pd_z/CeZr-O₂/SiO₂ catalysts.

3.3. XRD

XRD measurements were performed in order to verify the occurrence of ceria and ceria-zirconia mixed oxides phases. **Fig. 3** shows the XRD diffraction patterns of the Pd/CeO₂/SiO₂ and Pd_z/CeZr-O₂/SiO₂ catalysts. For all the prepared catalysts, no XRD peaks assignable to the PdO phase are visible, which may be due to the low loading of Pd (0.5 wt%) probably below the detection limit of standard XRD and/or the high dispersion of the PdO on the surface of the catalyst. The diffraction pattern of the Pd/CeO₂/SiO₂ sample shows associated peaks at $2\theta = 28.5, 32.9, 47.5$ and 56.3° , assigned to the ceria cubic phase [28,29]. Notably, for all the prepared catalysts presented, in addition to the broad peak corresponded to the amorphous silica phase, the same reflections as Pd/CeO₂/SiO₂ but all the ceria related peaks were shifted to higher 2θ positions. The higher intensity peak shifted from $2\theta = 28.6$ to 29.4° and no diffraction peaks related to zirconia phases were detected. Since the ion radius of Zr⁴⁺ (Zr⁴⁺ = 0.084 nm) is smaller than Ce⁴⁺ (Ce⁴⁺ = 0.097 nm) [18], these shifts toward higher 2θ values are indicative that ceria and zirconia formed a solid solution following the incorporation of Zr⁴⁺ into CeO₂ lattice,. These results are in agreement with several data in the literature which are focused on the solubility of ZrO₂ in CeO₂ and the formation of a Ce_xZr_{1-x}O₂ solid solution, which crystallographic structure depends on the value of x [18]. Furthermore, these results show that the introduction of palladium precursor during the CeZr-O₂/SiO₂ support preparation by sol-gel method did not affect the formation of the solid solution. However, what can be remarked is the decrease and the broadening of the related peaks which may be explained by the decrease in the particles size. On the other hand, Pd_z/CeZr-SiO₂ and Pd_d/CeZr-SiO₂ solids showed sharper and higher intensity peaks than Pd_{insitu}/CeZr-SiO₂ sample which suggested the growth and sintering of mixed oxide crystallites. The Scherrer equation was used to estimate the average crystallite size of the samples, the strongest diffraction peak of the Ce-Zr mixed oxide phase ($2\theta = 28.6^\circ$) is used in the

calculation. The mean particles size was 103, 92 and 68 nm on the Pd_o/CeZr-SiO₂, Pd_d/CeZr-SiO₂ and Pd_i/CeZr-SiO₂, respectively. The average crystallite size of mixed oxide in Pd_o/CeZr-SiO₂ catalysts is slightly larger than that of Pd_d/CeZr-SiO₂; this may be caused by the second calcination. These results suggest that aggregation or sintering of these particles occurs, and this may be explaining the slight decrease in S_{BET} in comparison with Pd_d/CeZr-SiO₂.

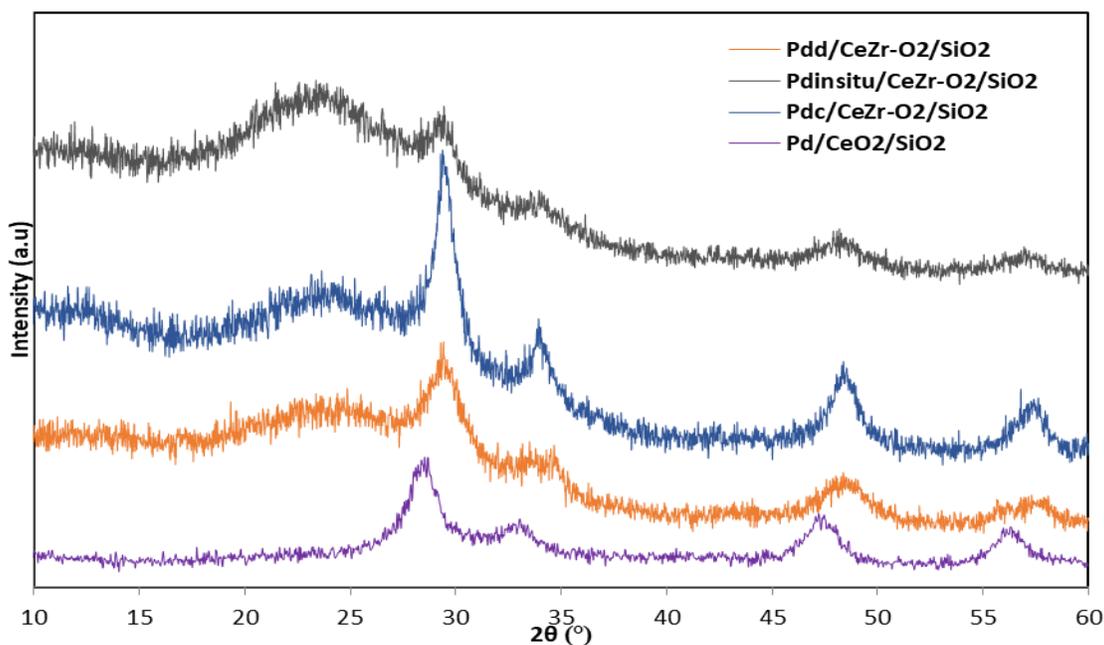


Fig. 3. XRD patterns of Pd/CeO₂/SiO₂ support and Pd₂/CeZr-O₂/SiO₂ catalysts.

3.4. TPD-NH₃ results

In order to study the influence of the method of palladium incorporation step in the surface acidity of the prepared support, NH₃-TPD is performed. TPD profiles are displayed in **Fig. 4**. The corresponding total acidity results are presented in **Table 2**.

It is established in the literature [21,22], that the ammonia desorption preceded in the temperature range from 25 to 600°C. The low-temperature peak around 100°C is ascribed to the coordinated ammonia to Lewis acid sites, which is prone to be desorbed at temperatures lower than 200°C. The medium-temperature peak is between 200 and 300°C. It corresponds to Bronsted-bonded ammonia, which is more thermally stable. These peaks can be assigned to NH₃ desorbing from weak acid sites. However, the high temperature peak observed above 500°C indicates a strong interaction of acid sites with NH₃ [21,22].

What can be grasped from **Fig.4** is that for the Pd_{insitu}/CeZr-O₂/SiO₂ catalyst, a distinct desorption peak can be recognized at 100°C with a shoulder at about 250°C which indicates that the catalyst possesses acid sites of weak and medium strength. Moreover, a small peak at 530°C was detected and was ascribed to strong acid sites. For Pd_o/CeZr-O₂/SiO₂ catalyst, three NH₃ desorption peaks are observed at around 70, 250 and 550 °C, corresponding to weak, medium and strong acid sites, respectively. The TPD profile Pd_d/CeZr-O₂/SiO₂ catalyst is consistent with that of Pd_o/CeZr-O₂/SiO₂ catalyst. Compared with Pd_o/CeZr-O₂/SiO₂ catalyst, the Pd_d/CeZr-

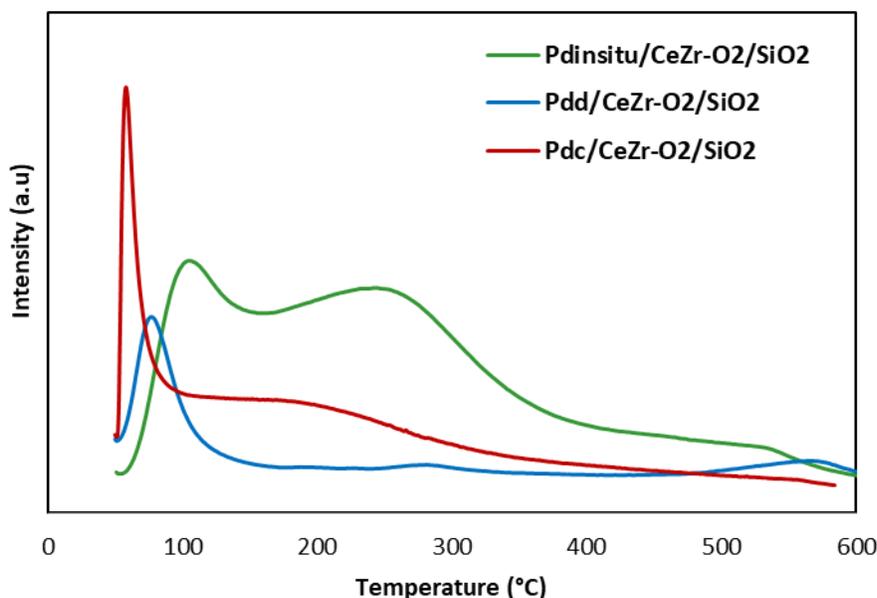
O₂/SiO₂ sample has a weak acid desorption peak (60°C) and a wide medium acid desorption peak ranged from 150 to 300°C, whereas the strong acid desorption peak almost disappears, indicating that the acidity is weakened. According to desorption peak temperatures, the acidity strength of the catalysts is observed to be dependent on the acid sites number. In fact, the number of acid sites follows this order: Pd_{insitu}/CeZr-O₂/SiO₂ > Pd_d/CeZr-O₂/SiO₂ > Pd_c/CeZr-O₂/SiO₂. Furthermore, these results were in agreement with the amount of ammonia desorbed which was 1183.2 μmol/g for Pd_{insitu}/CeZr-O₂/SiO₂ and decreased to 301.4 and 184.2 μmol/g for Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂, respectively.

It could be logically concluded that, for Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂, the higher dispersion observed by H₂-chemisorption should be attributed to the decrease in their surface acidity compared with the Pd_{insitu}/CeZr-O₂/SiO₂ catalyst.

Table 2

Total acidity of NH₃ and OSC of Pd_z/CeZr-O₂/SiO₂ prepared catalysts.

Catalysts	NH ₃ -TPD (μmol/g)	OSC (μmol/g)
Pd _{insitu} /CeZr-O ₂ /SiO ₂	1183.2	318.3
Pd _d /CeZr-O ₂ /SiO ₂	184.2	596.3
Pd _c /CeZr-O ₂ /SiO ₂	301.4	511.7



3.5. TPD-O₂ results

Fig. 5 shows the results of TPD-O₂ experiment over the Pd_z/CeZr-O₂/SiO₂ catalysts while the values of the O₂ consumption are shown in **Table 2**. From **Fig. 5** and **Table 2**, it can be seen that the TPD profiles of all catalysts display four peaks of oxygen desorption when the temperature is raised to the range of 30–1000°C. The two small desorption peaks at low temperatures (below 100°C) are attributed to the physically adsorbed oxygen (O₂). The desorption peaks in the temperature range from 200 to 500°C can be assigned to the chemisorbed surface active oxygen species (O₂⁻, O⁻) and to the oxidation of stable metallic palladium species[23]. Moreover, all catalysts exhibit a peak at around 640, 635 and 600°C, respectively, for Pd_{insitu}/CeZr-O₂/SiO₂, Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ which are attributed to the decomposition of PdO species [23]. The shift to higher temperature for Pd_{insitu}/CeZr-O₂/SiO₂ than the corresponding temperature observed for Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ catalysts, indicating that the addition of the palladium precursor by impregnation on CeZr-O₂/SiO₂ dried support would obviously enhance the thermal stability of PdO. Evenly, these results correlate with changes observed in the size of the PdO particles. Small PdO particles on the support tend to have stronger interactions, which shifts the O₂ desorption peak to higher temperature.

Furthermore, for the Pd_d/CeZr-O₂/SiO₂ another peak at 850°C is observed and is ascribed to desorption of support bulk lattice oxygen. It is worth pointing out that the oxygen desorption area and the amount of O₂ desorption depend obviously on the preparation method and the palladium incorporation step. In fact, as can be detected from **Table 2**, the Pd_d/CeZr-O₂/SiO₂ catalyst has the highest amount of surface oxygen species and lattice oxygen (596.3 μmol/g). These results indicate that the addition of the palladium precursor by impregnation on CeZr-O₂/SiO₂ dried support is the best method to have the highest OSC. This should be due to the strong interaction palladium/support on Pd_d/CeZr-O₂/SiO₂ catalyst compared to Pd_{insitu}/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ catalysts, issued from the two others synthesis processes. In effect, according to the literature [24,25], the electronic charge distribution between palladium, cerium and zirconium atoms can modify the Ce–Zr–O bond, and consequently the amount of surface oxygen on CeO₂-ZrO₂/SiO₂ support. This modification can be explained by the partial occupation of vacant Ce sites with palladium, which will create additional oxygen vacancies on the surface of the Ce⁴⁺- O₂ fluorite oxide. In order to verify these results, the palladium-support interaction is examined by the XPS characterization.

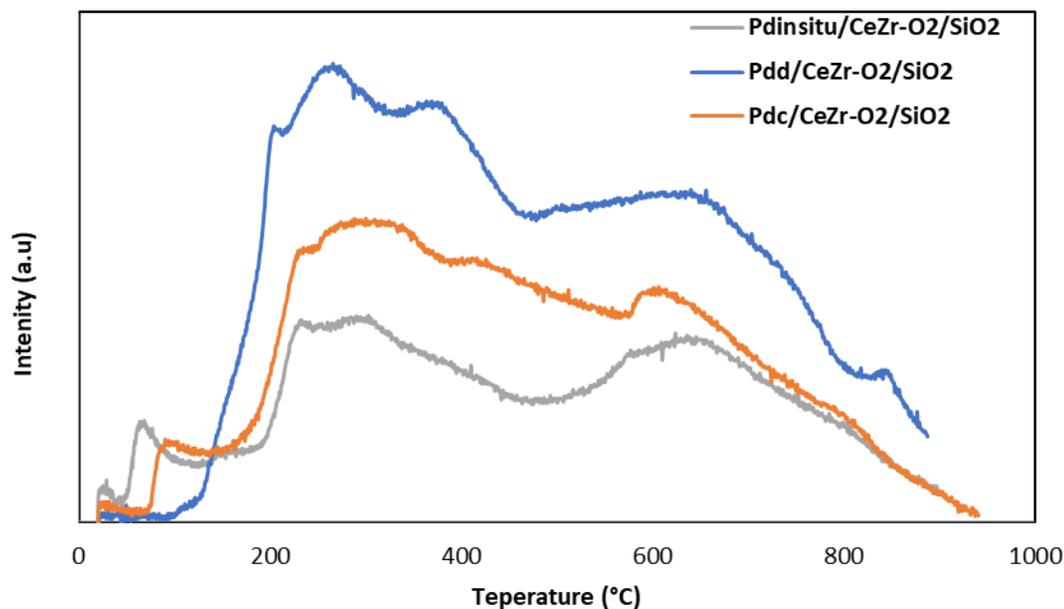


Fig. 5. TPD-O₂ over Pd_z/CeZr-O₂/SiO₂.

3.6. Surface chemical state

Table.3: XPS data of the catalysts prepared by different palladium introduction step.

Sample	BE Pd 3d _{3/2} (eV)	BE Pd 3d _{5/2} (eV)	Oxidation state	BE O 1S (eV)	BE Zr 3p (eV)	BE Ce 1S (eV)
Pd _{insitu} /CeZr-O ₂ /SiO ₂	340.0	336.9	Pd ²⁺	530.8	181.5	881.7
Pd _d /CeZr-O ₂ /SiO ₂	339.8	337.7	Pd ²⁺	530.5	183.4	881.6
Pd _c /CeZr-O ₂ /SiO ₂	342.9	337.1	Pd ²⁺	532.8	183.3	881.5

The XPS analyses of the prepared catalysts were carried out to investigate the relationship of surface species and valence state of the active phase with the catalytic behavior and the related data are gathered in **Table 3**. XPS results indicated that palladium is only present as PdO (Pd²⁺) species for all catalysts, which suggest that CeO₂-ZrO₂ based systems can stabilize Pd species in their oxidized state through an interaction via oxygen surface [26]. Moreover, it is known in the

literature that the phase with lower surface tension (PdO) tends to encapsulate the phase with higher surface tension (Pd⁰) [27], thus the absence of metallic Pd contribution may be explained also by the encapsulation of Pd⁰ by PdO phase.

From **Table 3**, the Pd3d_{5/2} binding energies of the Pd_z/Ce_xZr_{1-x}O₂/SiO₂ catalysts fall in the range of 336.9–337.7 eV which is higher than the habitual Pd3d_{5/2} binding energies (336.4 ± 0.1 eV). This increase can be related to the interaction between PdO and the CeZr-O₂/SiO₂ support [27]. Furthermore, the relatively high Pd3d_{5/2} BE on the Pd_d/CeZr-SiO₂ catalysts (337.7 eV) indicates that the incorporation of palladium precursor by impregnation on dried CeZr-O₂/SiO₂ support enhances the interaction between Pd species and the support, making the Pd species with higher oxidation state more active for methane combustion [27,30]. These results find resonance in those described in the literature [31]. In fact, a strong metal–support interaction is found especially on supports with mobile oxygen such as TiO₂, ZnO, ZrO₂, ZrO₂–CeO₂ and CeO₂ due to oxygen transfer from the support to the active sites which favor thereby the re-oxidation process of the active PdO species on the catalytic surface. Moreover, the BE of Pd significantly depends on the particle size of PdO and the BE value of Pd3d_{5/2}. It increases with decreasing PdO particle size [32]. Remarkably, in small particles, the internal layers are more accessible to radiation than in the larger ones. Thus, the relative highly dispersed palladium oxides particles (34% for Pd_d/CeZr-SiO₂) are capable of re-oxidation during oxygen contact. These results are in accordance with XRD and H₂-chimisorption results. Moreover, from the data in **Table 3**, the BE of Zr 3d_{5/2} are between 181.7 and 181.8 eV and the BE of Ce 3d_{5/2} are between 881.9 and 882.1 eV. These results indicate that the majority of ZrO₂ and CeO₂ form a solid solution Ce_xZr_{1-x}O₂ [33], which in a good agreement with XRD results.

3.7. Catalytic activity

The catalytic performance of the prepared catalysts is investigated in methane combustion. To compare the catalytic activities, T50 and T90 (the temperature needed for 50% and 90% methane conversion, respectively) over the catalysts were estimated from **Fig. 6**.

From the data in **Table 4 and Fig. 6**, it can be seen that the Pd/SiO₂ catalyst exhibits low activity for methane combustion (23% at 500°C). However, the presence of cerium and zirconium oxides would obviously improve the thermal stability of PdO phase of the Pd/SiO₂ catalysts and enhance the catalytic activity, indicating that the introduction of ceria and zirconia and also the insertion of Zr to ceria lattice and the formation of solid solution are favorable for methane combustion. This is well in agreement with our previous research. In fact, I. B. Said et al. [18] show that the addition of an appropriate loading of Ce and Zr to the Pd/MCM-41 catalyst can improve significantly its catalytic activity for methane combustion.

Furthermore, the support CeZr-O₂/SiO₂ prepared by sol-gel method shows a very low activity in methane combustion (< 10% at 500°C). Notably, with the incorporation of palladium, the activity of catalysts is remarkably improved and the conversion curves shift to lower temperatures, especially for the catalysts prepared by impregnation on dried and calcined CeZr-O₂/SiO₂ support. It is well known, that PdO species are the active centers for methane combustion reaction [18], so it was understandable that Pd_z/CeZr-O₂/SiO₂ prepared catalysts exhibits a higher reaction activity.

On the other side, the method of palladium incorporation step seems to affect greatly the catalytic behavior of Pd_z/CeZr-O₂/SiO₂ materials. Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ catalysts show practically the same methane conversion, whereas a substantial decrease in the activity is observed in the Pd_{insitu}/CeZr-O₂/SiO₂ sample. For example, the T50 was 360 and 368 °C over Pd_s/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂, respectively, which was much lower than that over Pd_{insitu}/CeZr-O₂/SiO₂ sample (T50 = 434 °C), as shown in **Table 4**. Therefore, one has the following catalyst ranking: Pd_c/CeZr-O₂/SiO₂ ≈ Pd_d/CeZr-O₂/SiO₂ > Pd_{insitu}/CeZr-O₂/SiO₂. This result suggests that the addition of palladium precursor by impregnation on CeZr-O₂/SiO₂ calcined or dried support seems to be an adequate method to improve the catalytic activity in methane combustion.

Xia et al. [36] considered that the activity of a catalyst was influenced by several factors, such as surface area, surface oxygen species, support acidity, dispersion of the active phase and reducibility. According to the above characterization results, Pd_c/CeZr-O₂/SiO₂ and Pd_d/CeZr-O₂/SiO₂ catalysts have the larger specific surface area; good dispersed state of PdO particles on the support's surfaces, more abundant active surface oxygen species and active Pd²⁺ cationic species. These results are in line with the literature [36], a catalyst with larger specific surface area can expose more active facets in the oxidation reaction. Thus, the differences in the catalytic performance could probably be attributed to the differences in the number of exposed active sites in Pd_c/CeZr-O₂/SiO₂ and Pd_d/CeZr-O₂/SiO₂ comparing to Pd_{insitu}/CeZr-O₂/SiO₂.

Additionally, it is more accurate to use the turnover frequencies (TOFs) for evaluating the inherent catalytic activities of the prepared catalysts, as summarized in **Table 2**. It is clearly observed that the Pd_{insitu}/CeZr-O₂/SiO₂ sample exhibit a relatively high TOF (32.6 h⁻¹), in the combustion of methane at 325 °C, followed by Pd_c/CeZr-O₂/SiO₂ (27.2 h⁻¹) and Pd_d/CeZr-O₂/SiO₂ (12.3 h⁻¹). In fact, it is not surprising that the Pd_{insitu}/CeZr-O₂/SiO₂ catalyst with a lower dispersion (4%) shows a higher activity per site, this result probably due to the growth of palladium particle size compared to other catalysts. Indeed for a given quantity of metal, an optimal size of the particles seems to be essential to maximize the activity, a similar conclusion was advanced by L.M.T. Simplicio et al. [34].

The other important conclusion that can be drawn is that the method of palladium addition step leads to different metal-support interaction which affects greatly the chemical state of palladium and the acidity strength, known as a key factor in the catalytic behavior of Pd based catalysts. Therefore, the relatively high Pd3d_{5/2} BE on the Pd_d/CeZr-O₂/SiO₂ catalysts (337.7 eV) suggest that the incorporation of palladium precursor by impregnation on calcined CeZr-O₂/SiO₂ support enhance the interaction between Pd species and the support which contribute to the slight enhancement in methane conversion comparing to Pd_c/CeZr-O₂/SiO₂ catalysts,

On the other side, improved OSC (**Table 2**) revealed to be beneficial to the catalytic performance of Pd based catalyst, since it favors the methane oxidation. Thereby, the activity of Pd_z/CeZr-O₂/SiO₂ catalysts follows the same tendency as that of oxygen storage capacity (OSC). The Pd_c/CeZr-O₂/SiO₂ and Pd_d/CeZr-O₂/SiO₂ catalyst have the highest OSC with a slight preference for Pd_d/CeZr-O₂/SiO₂ sample, meaning that it can provide the richest surface active oxygen species that allows the reactant to diffuse and undergo surface reactions and improve, consequently its catalytic performance. In fact, Martin and Duprez [35] also demonstrated exceptional mobility of both surface and bulk oxygen over CeO₂, and found that the presence of metal particles on the CeO₂ significantly increases the oxygen mobility between 300 and 450 °C.

So that, the slight increase in methane conversion for Pd_s/CeZr-O₂/SiO₂ may be explained by the increase of oxygen mobility at the catalyst surface.

In addition to OSC, the acid–base properties of the materials performed by NH₃-TPD must then be taken into account to explain the difference observed in methane conversion. These results prove that the amount of ammonia desorbed by Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ is very low than obtained in Pd_{insitu}/CeZr-O₂/SiO₂, meaning that Pd_d/CeZr-O₂/SiO₂ and Pd_c/CeZr-O₂/SiO₂ have a weak acidity in comparison with Pd_{insitu}/CeZr-O₂/SiO₂.

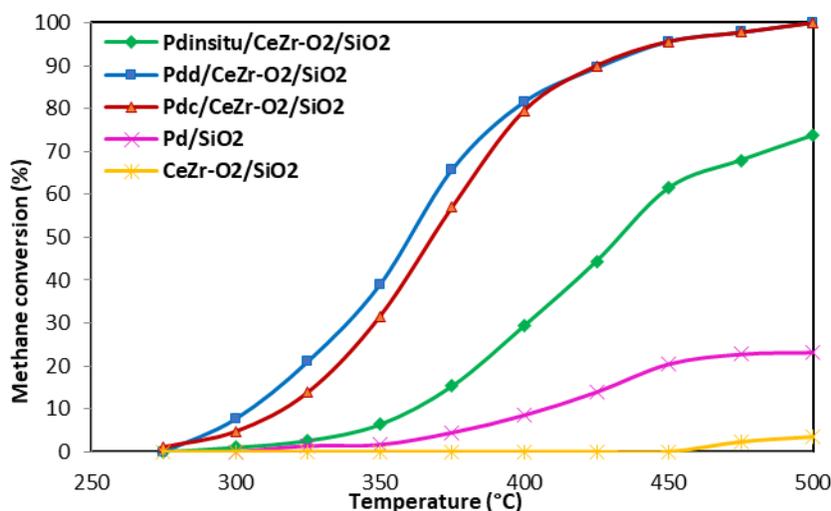


Fig. 5. Effect of palladium addition step on methane combustion performance of Pd_z/CeZr-O₂/SiO₂ catalysts.

Table 4

Light-off temperature and turnover number at 325°C of the Pd_z/CeZr-O₂/SiO₂ catalysts.

catalysts	T10 (°C)	T50 (°C)	T90 (°C)	TOF ^a (h ⁻¹)
Pd _{insitu} /CeZr-O ₂ /SiO ₂	362	432	-	32.6
Pd _d /CeZr-O ₂ /SiO ₂	305	361	428	12.3
Pd _c /CeZr-O ₂ /SiO ₂	316	368	427	27.2
Pd/SiO ₂	405	-	-	-
CeZr-O ₂ /SiO ₂	-	-	-	-

^a Turnover frequency (TOF) at 325°C.

4. Conclusion

In this work, the preparation of the Pd_z/(Ce_xZr_{1-x}O₂)/SiO₂ catalysts with different palladium addition routes has been investigated through different characterization techniques and their performance in methane oxidation is studied. The sol-gel process allows producing a mesoporous catalyst with relatively high specific surface area in particular for Pd_d/CeZr-O₂/SiO₂ sample which showed the highest specific surface area and the largest pore volume. The XRD patterns revealed the formation of Ce_xZr_{1-x}O₂ solid solution for all catalysts following the substitution of Ce⁴⁺ by Zr⁴⁺ ions in the ceria lattice. Furthermore, the NH₃-TPD shows significant changes in surface acidity. The total surface acidity of the Pd_{insitu}/CeZr-O₂/SiO₂ catalyst is remarkably increased compared to the other catalysts, which is especially unfavorable for palladium dispersion. The O₂-TPD results indicate that the palladium addition step catalysts do not have the same effect on the desorption behavior of surface and bulk oxygen. Obviously, the surface oxygen desorption capacity and the mobility of lattice oxygen increase when the palladium is incorporated after the preparation of the Ce_xZr_{1-x}O₂/SiO₂ support (dried or calcined), which is beneficial to the PdO dispersion and the catalytic performance. Moreover, the Pd3d_{5/2} photopeak binding energy increased following the order Pd_c/CeZr-O₂/SiO₂ > Pd_d/CeZr-O₂/SiO₂ > Pd_{insitu}/CeZr-O₂/SiO₂. This seems to be due to the strong interaction between PdO and the CeO₂-ZrO₂ solid solution and the decrease in PdO particles sizes.

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