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Complete catalytic oxidation of methane over Pd/CeO_2–Al_2O_3: The influence of different ceria loading

R. Ramírez-López [a], I. Elizalde-Martinez [a,b], L. Balderas-Tapia [a,*]

[a] Instituto Politécnico Nacional, Departamento de Ingeniería Química Industrial, ESIQIE, Av. IPN s/n, Edificio 7, 1er piso, UPALM, 07738 México, D.F., Mexico
[b] Universidad Nacional Autónoma de México, Facultad de Química, Ciudad Universitaria, 04510 México, D.F., Mexico

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ABSTRACT

Five kinds of mixed supports of CeO_2–Al_2O_3 were prepared by sol–gel method by varying the amount of ceria in the support from 2 to 50 wt.%. These supports were impregnated with palladium nitrate in order to obtain the catalytic samples. The effect of different ceria loading on Pd/CeO_2–Al_2O_3 catalysts and supports was investigated by physical characterization such as surface area measurements and XRD analysis. Additionally, TPR profiles of supports and Pd-containing catalyst were recorded. Reduction of surface area was observed for samples with high amount of ceria. For catalytic support with the highest ceria loading well crystallized ceria was observed whereas the other samples showed amorphous phases. TPR results have evidenced the enhancement of reduction of ceria in the supports by addition of precious metal although reduction of catalytic samples requires higher temperature as the amount of ceria in the support is higher. The results of oxidation of methane over Pd/CeO_2–Al_2O_3 confirm the suppression of the catalytic activity for samples containing high ceria loading, although such degree of depression depends also on cerium oxides present in the catalytic support.

1. Introduction

Gasoline is a petroleum product which has been used as fuel in internal combustion engines for several decades. However, recently due to stringent conditions imposed regarding to pollutant emissions, new alternative fuels such as natural gas, composed mostly of methane (>90 mol%) has been proposed to substitute the gasoline fuel [1]. Natural gas represents the cleanest alternative of the available fossil fuels. It is found to be one of the most environment friendly fuel as natural gas powered vehicles emit 85% less NO_x, 70% less reactive HC's, and 70% less CO than similar gasoline powered vehicles [2]. This fact has impacted in the increase of the number of vehicles running with natural gas [3] and governments in both developed and developing countries have promoted the use of natural gas for two main reasons: reduction of dependence of fuel oil and because of its environmental benefits [1]. On the other hand, manufacturers have paid more attention in improving those engines for using more rationally the gas fuel. Low efficiency can be expected to be achieved in the engines for natural gas because methane emissions are difficult to be oxidized under conditions typically found in internal combustion engines. Exhaust gases from natural gas engines typically contain 7 vol.% of CO_2, 14% water, 5% oxygen and from 500 to 5000 ppm unburned methane [4] and their temperatures vary between 300 and 550 °C. In this range of temperature, is impossible to convert the unburned methane to CO_2 as has been early reported by Yu Yao [5]. Thus the benefits of natural gas are offset by relatively high emissions of unburned methane which although is non-toxic and almost photochemically inert, its removal is mandatory because its greenhouse effect is even more adverse than CO_2 [4,6–8]. By operating the engine at lower concentrations of oxygen than stoichiometric, methane emissions are produced. In order to enhance the use of lean methane burning conditions usually have been employed. At higher concentrations of oxygen, insignificant amounts of nitrogen oxides (NO_x) have been observed [7]. During normal operation of engines, variations of methane/oxygen ratio can occur hence conditions of reaction vary from lean to rich methane concentrations. In order to do methane emissions abatement efficiently, after-treatment has been successfully used. It has been established that a catalyst able to treat exhausted gases of natural gas vehicles (NGV) must have the following characteristics: high efficiency using very diluted feedstreams (less than 1000 ppm of methane) and high oxygen concentrations, low light-off temperature at high space-velocities, high thermal stability and resistance to deactivation by water and sulfur oxides (SO_x). A catalyst proposed for such a purpose is one composed of noble metal such as palladium, platinum or rhodium, and alloys of these metals [1,9]. The noble metal has the role of oxidation of hydrocarbons [5] and it has been reported that palladium is one of the most active precious metals for oxidation of methane due to

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[*] Corresponding author. Tel.: +52 55 5729 6000x55293; fax: +52 55 5586 2728.
E-mail address: lbalderast@ipn.mx (L. Balderas-Tapia).

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its lowest light-off temperature although on the other hand it has been recognized that this metal is very sensitive to poisoning by water and traces of SO_x [10,11]. The most common supports are alumina and zirconia [11] although other supports have been explored in order to improve the performance of catalysts. Rare earths are typically used as promoters. Among several rare earths, ceria is the most common promoter, since its advantages which are briefly mentioned: enhances the dispersion of the noble metal, promotes noble metal oxidation and reduction during reaction conditions, increases thermal stability of support, stores and releases oxygen, hydrogen and sulfur, form surface and bulk vacancies, suppresses partial oxidation products (carbon monoxide), forms intermetallic compounds (M–Ce), interacts synergistically with palladium favoring the methane oxidation at low temperature and improves the performance of Pd-containing materials at low and at high temperatures [12–15]. Also ceria is compatible with both palladium as well as alumina. Traditionally alumina support has been prepared by sol–gel method in order to obtain high specific surface areas and after its preparation addition of ceria is carried out with cerium salt-derived by means of impregnation technique. It has been proposed previously that as the temperature of calcinations is high or the amount of ceria in the support is relatively high, the crystal size of ceria increases provoking sinterization, although the size of the crystal cannot be greater than the size of the pore [16], which can be controlled by sol–gel method. Preparing the supports together with the promoter using the sol–gel method have other advantages such as increasing the amount of promoter keeping relatively high specific surface areas, better interaction between support and metal, high homogeneity, thermal stability for supported catalysts and synergetic effect between promoter and metal [15,17].

In a previous work [18], a series of palladium promoter alumina-supported catalyst prepared by sol–gel method were tested in the oxidation of methane and it was observed that cerium plays an important role in the oxidation of such a hydrocarbon because it provides the oxygen when the oxygen/methane ratio was lower than 2, that is under deficient oxygen concentration. Also it was observed that samples with higher cerium content are more active toward oxidation of methane under stoichiometric and oxygen deficient mixture. This fact apparently is contradictory with previous reports [6] where it was stated that ceria has a detrimental effect over both platinum and palladium-supported catalysts. Probably the explanation of these different behaviors can be related to the preparation method of support and amount of cerium which allows for better interaction between support and metal [8] although other factors could be involved [17]. On the other hand, it has been observed that catalytic samples with high ceria loading in the support (50 wt.%) prepared by sol–gel method and platinum as active phase perform better than samples with lower ceria loading [17]. In order to investigate the effect of ceria loading in catalysts with palladium as active phase in this work, the preparation of support samples by sol–gel method is reported as well as the effect of addition of precious metal over support. The aim of this work was to investigate the influence of ceria loading (2, 5, 10, 15 and 50 wt.%, CeO_2) in CeO_2–Al_2O_3-supported Pd catalyst prepared by the sol–gel method in the complete oxidation of methane at low temperature (lower than 550 °C).

2. Experimental

2.1. Preparation of materials

2.1.1. Preparation of supports

Five kinds of catalytic mixed supports were prepared by using the sol–gel method. Aluminum alcoxide (Aldrich, 98%) was previously dissolved into isopropyl alcohol and a solution of cerium nitrate (Aldrich, 99%) was added at specific concentrations in order to obtain the supports with different ceria loading (2, 5, 10, 15 and 50 wt.%, theoretical values) keeping the temperature constant at 5 °C and mixing vigorously during addition. After gelation of supports, they were dried at 100 °C overnight and calcined at 600 °C under oxygen atmosphere using a rotatory furnace with the following heating schedule: from 25 to 200 °C heating rate 1 °C/min, hold at this temperature for 2 h; from 200 to 400 °C heating rate 1 °C/min, hold at this temperature for 1 h; and from 400 to 600 °C heating rate 1 °C/min, hold at the final temperature for 7 h. Finally, the samples were cooled at room temperature.

2.1.2. Pd-containing catalysts

The supports were impregnated with nitrate of palladium (Aldrich, 99%) diluted in water with the appropriate concentration of metal in a rotary vapor at 100 °C. The five samples were dried at 100 °C overnight and calcined at 600 °C using a rotatory furnace with the same heating schedule used for supports calcination. The five samples were referred as Pd/NAC*x*, where *x* is 1–5 for the theoretical ceria loading of 2, 5, 10, 15 and 50 wt.%, respectively.

2.2. Characterization

2.2.1. Morphological analysis

Specific surface areas, mean pore diameters and pore volumes were measured by N_2 adsorption at 77 K using a Micromeritics ASAP 2000 apparatus. Results are reported in Table 1.

2.2.2. X-ray analysis

XRD analysis was recorded in a Phillips X-ray generator. CuK_α X-rays, having a wavelength (λ) of 1.5406 Å was used as X-ray source. Particle size of crystalline ceria was determined by Scherrer's equation for the sample where the crystals were observed, using the peaks at $2\theta = 28.5°$ [15].

2.2.3. Chemical analysis

Chemical analysis was made by inductively coupled plasma-atomic emission spectroscopy (ICP).

A Spectra 220 FS Varian apparatus was employed for this purpose. The composition of the five samples is reported in Table 2.

2.2.4. Temperature programmed reduction (TPR)

TPR experiments were carried out in a home-made apparatus, which includes a quartz reactor fitted with a thermo conductivity

Table 1
Morphological data of samples.

Catalytic sample	SSA (m^2/g)	PV (cm^3/g)	dp (Å)	CeO_2 crystal size (Å)
Pd/NAC1	327	0.88	107	n.d.
Pd/NAC2	359	1.17	130	n.d.
Pd/NAC3	319	1.03	130	n.d.
Pd/NAC4	203	0.66	130	n.d.
Pd/NAC5	86	0.13	59	82

n.d.: not detected.

Table 2
Chemical composition of catalytic samples.

Catalytic sample	Alumina (wt.%)	Ceria (wt.%)	Palladium (wt.%)
Pd/NAC1	97.76	2.06	0.18
Pd/NAC2	94.40	5.38	0.22
Pd/NAC3	89.36	10.47	0.17
Pd/NAC4	83.57	16.25	0.18
Pd/NAC5	52.08	47.80	0.12

detector (TCD) housed in an electric furnace. The internal diameter of reactor was 15 mm. Temperature was raised from 25 up to 600 °C by steps of 10 °C/min and reduction was carried out by a mixture of hydrogen–argon (10:90 vol.%) passing through the catalytic bed. Hydrogen uptake was recorded as a function of temperature for each support and catalyst.

2.2.5. Catalytic tests

Catalytic activities of the Pd catalysts for methane oxidation were investigated using the same reactor system employed for TPR measurements operated at atmospheric pressure. A thin layer of powder catalyst with particle size of 0.125 mm was loaded into the reactor. A gaseous mixture of 0.5 vol.% CH_4, 1 vol.% O_2, and 98.5 vol.% helium was fed to the quartz tube at a space-velocity of 52,000 h^{-1}. The reactor was equipped with a thermocouple centered inside the reactor. Reaction feed and products were analyzed on line with a HP chromatograph 5610 equipped with a thermal conductivity detector. Temperature studied for methane conversion ranged from 300 to 600 °C, raising the temperature by steps of 10 °C. At lower temperatures the conversion of methane was insignificant.

3. Results and discussion

3.1. Characterization of support

3.1.1. Morphology and XRD measurements

Table 1 reports the specific surface area, mean pore sizes and pore volumes for all the supports calcined at 600 °C. High specific surface areas (SSA) were obtained for samples containing lower amounts of ceria. However, considerable reduction of SSA was observed for the sample with the highest ceria loading. This fact can be attributed to pore plugging by ceria crystals formed under conditions employed during calcinations of supports and also due to ceria loading.

XRD diffraction patterns of samples containing lower ceria loading than 50 wt.% are reported in Fig. 1. These diffraction patterns have been shifted vertically in ascending order of ceria loading in the same figure because they show similar patterns. These samples exhibit amorphous phases at the temperature of calcinations used. It can be expected different ceria oxides to be present in the supports including those non-stoichiometric ones. The support with the highest ceria loading (50%) shows ceria diffraction patterns well defined in region of 2θ values = 28.5°, 33°, 47.5°, 56.3°, 59.0° and 69.5°, as displayed in Fig. 2. The crystal size of ceria for this sample is within the range reported in the literature for samples containing high ceria loading calcined at low temperature [19]. This last sample has the lowest SSA which confirms the trend of ceria for plugging the pore of support at high loading. This last feature could be detrimental for methane oxidation since at lower SSA available the less the accessible sites during rapid oscillation in the composition of the engine exhaust [20] although diminution of catalytic activity is not simply due to the change of the surface area [21].

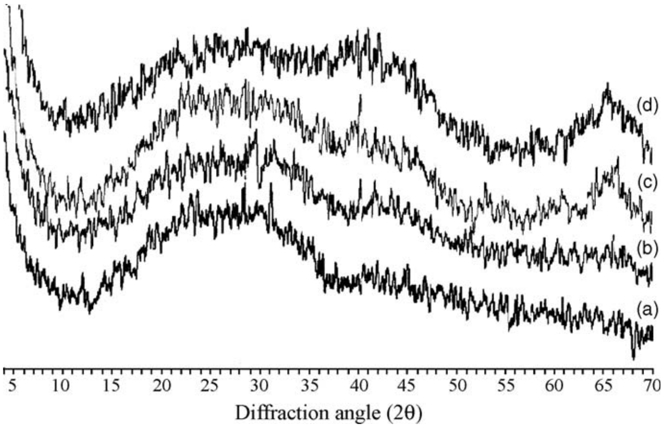

Fig. 1. XRD diffraction patterns of CeO_2–Al_2O_3 samples (wt.% ceria): (a) 2, (b) 5, (c) 10, and (d) 15.

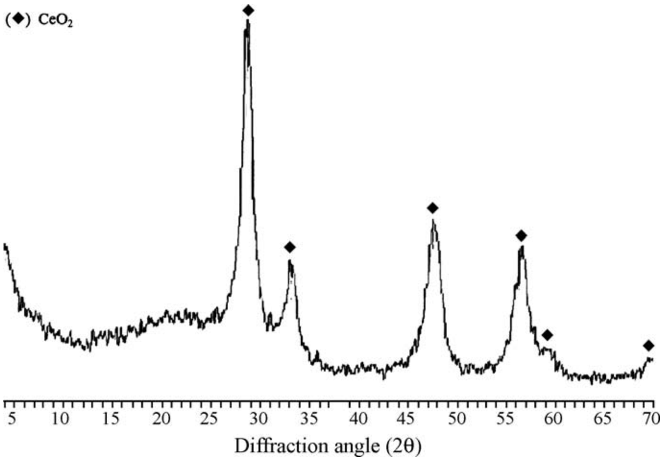

Fig. 2. XRD diffraction patterns of CeO_2–Al_2O_3 sample with 50 wt.% ceria.

3.1.2. Temperature programmed reduction of supports

Fig. 3 shows TPR profiles as a function of temperature of the CeO_2–Al_2O_3 supports calcined at 600 °C. The samples with 2 and 5 wt.% of ceria (a and b) do not show any peak indicatory of ceria reduction due to low amount of rare earth which is distributed in bulk of support and at the surface. The support with 10 wt.% ceria (c) shows a broad peak at 440 °C, which can be attributed to reduction of oxygen of superficial cerium oxide. At the same temperature the sample with 15 wt.% ceria (d) shows a peak although it is overlapped with a shoulder at *ca.* 490 °C. In the sample with highest amount of ceria loading (e) the peak at 440 °C is shown as a shoulder which is overlapped with a broad peak whose maximum is around 580 °C.

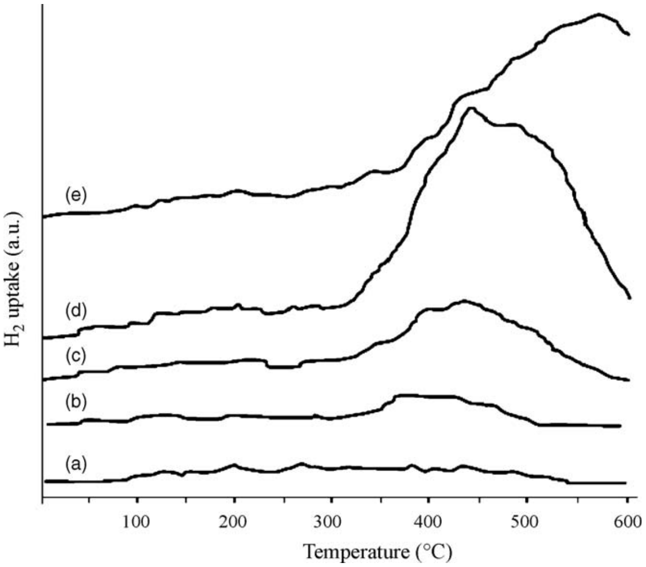

Fig. 3. TPR profiles of the supports containing different ceria loading (wt.%): (a) 2, (b) 5, (c) 10, (d) 15, and (e) 50.

3.2. Characterization of catalysts

3.2.1. Chemical composition of catalysts

Previously, it has been reported that in case of platinum-containing catalyst, a sample of alumina with 50% Ce loading performs better than samples having lower ceria loading [17]. Ceria can be used as catalyst or can be used as co-catalyst for the complete oxidation of methane. In order to investigate this possibility we have added the lowest palladium loading for sample Pd/NAC5 as seen in Table 2.

3.2.2. Temperature programmed reduction of Pd-containing catalysts

Fig. 4 shows the hydrogen uptakes as a function of temperature obtained for the Pd/NAC*x* catalysts calcined at 600 °C. The various traces have been shifted vertically for clarity. The effect of Pd on TPR of supports is indeed evident. It is observed in Fig. 1 that the higher the content of ceria in the catalyst, the higher hydrogen consumption [5], which is indicatory of better mobility of oxygen species from the catalyst surface, which in turn could favor the methane conversion although also can provoke excessive oxidation of the noble metal and lower conversion of methane as a consequence. This figure shows that catalytic samples with 2 and 5 wt.% ceria loading (a and b) are only reduced at temperatures lower than 300 °C. The peaks are probably associated with absorbed oxygen on the bare amorphous alumina sites [20,22] since Pd does not show any peak in TPR profiles [15]. The main peak in this region near 120 °C diminishes for ceria loading higher than 2 wt.% but lower than 15 wt.%, from which the opposite behavior is observed. Multiple peaks have been reported in this region by Yao and Yao [20], with addition of precious metal to CeO_2–Al_2O_3. At temperatures higher than 300 °C samples Pd/NAC3 and Pd/NAC4 (c and d) show a characteristic peak which is in line with previous reports [16]. These peaks are associated with the reduction of surface oxygen of ceria. For the sample with 10 wt.% ceria loading, a peak around 400 °C is attributed to the reduction of the surface oxygen of CeO_2. On the other hand, for the sample with 15 wt.% ceria loading two peaks are observed, one at *ca.* 380 °C and the other near 420 °C although these two peaks are overlapped and their resolution is not sharp. It can be inferred that those two peaks are originated from different cerium oxides and probably the peak at 380 °C could be associated with a non-stoichiometric cerium oxide [15,20]. Since non-stoichiometric ceria interacts synergistically with palladium [15] high activity for methane oxidation can be expected for this sample. As can be seen the peak attributed to ceria reduction of Pd/NAC4 is moved toward higher temperature respect to the sample with 10 wt.% ceria which could be due to higher ceria loading as reported previously [22]. For the sample containing the highest amount of ceria (e), a broad peak at near 480 °C can be attributed also to CeO_2 reduction. This peak is overlapped with another peak at 380 °C, which is observed as a shoulder. This behavior could be attributed to transformation of the different cerium oxides. Because the amount of ceria is high in the last catalyst, the reduction of oxygen is difficult after reduction of surface capping oxygen and higher temperatures are required in order to reduce completely this sample. A detrimental effect of higher ceria loading on methane oxidation can be expected because reduction of SSA and excessive oxidation of noble metal.

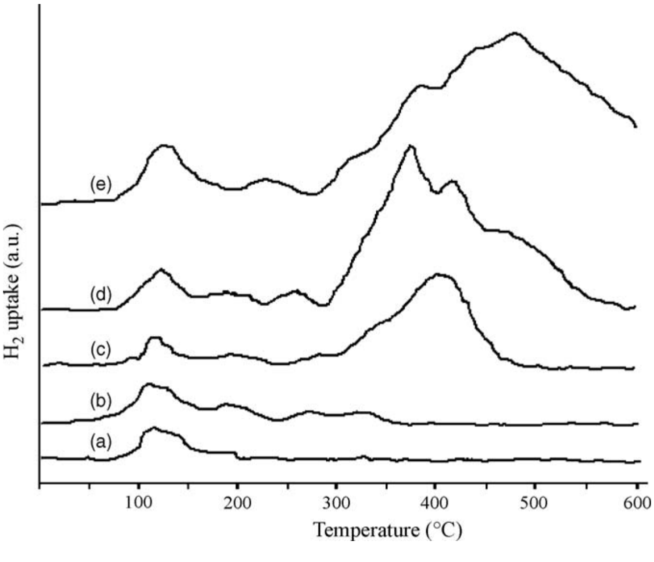

Fig. 4. TPR profiles of Pd/CeO_2–Al_2O_3 catalysts calcined at 600 °C (wt.%): (a) 2, (b) 5, (c) 10, (d) 15 and (e) 50.

3.2.3. Catalytic tests

It has been pointed out in the literature that at low temperature the PdO species is the active phase for oxidation of methane [1,11,23]; on the other hand, it has been stated that both Pd and PdO species are necessary for such a purpose [10,11,24,25]. During reaction it has been proposed a change of state oxidation from PdO to Pd although such a change occurs at temperatures higher than 600 °C for 1% oxygen concentration [11]. Also, it has been reported that water strongly inhibits methane oxidation rates by titrating both vacancy and activated oxygen surface sites required for methane activation [24]. In order to avoid these detrimental effects two possibilities can be carried out: (1) increase the temperature reaction and (2) modify the support. Keeping low temperatures in the catalytic combustion of methane is the main reason for its use, hence modifying the support can help to circumvent the detrimental effect of water. Fig. 5 shows the catalytic methane oxidation as a function of temperature over Pd/NAC*x* catalysts as has been done in this work. The sample containing 15 wt.% ceria (Pd/NAC4) seems to be a bit more active below 425 °C but Pd/NAC1 sample shows the lowest light-off temperature reaching total conversion at the lowest temperature, followed by Pd/NAC4, Pd/NAC2, Pd/NAC3 and Pd/NAC5. As can be seen, although Pd/NAC4 sample has a great amount of cerium oxides it performs better than those containing 5 and 10 wt.% ceria. The last observation could confirm the presence of non-stoichiometric cerium oxides in Pd/NAC4 catalyst which exhibits synergistic effect with palladium, that is, probably the cerium oxide permits partial reduction of precious metal in the bulk of PdO providing the reduced metal over which methane is activated, as has been reported [1,10,24,25]. Below conversion of 60% Pd/NAC4 is still the more active catalyst and Pd/NAC2 shows performances more similar to those of Pd/NAC3 sample whereas the catalyst with the highest ceria loading shows the poorest behavior in the complete oxidation of methane.

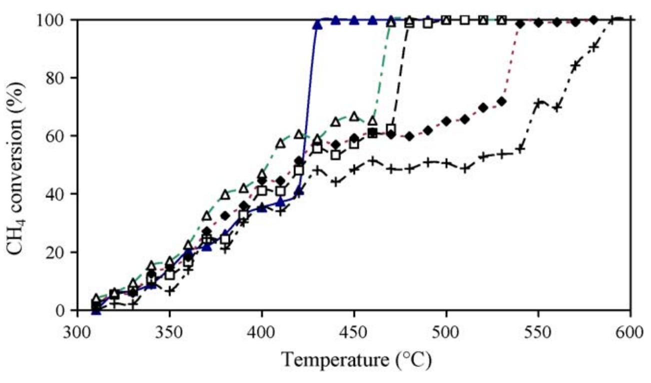

Fig. 5. Conversion of methane over Pd/CeO_2–Al_2O_3 catalysts as a function of temperature in a feedstream containing 0.5 vol.% CH_4, 1 vol.% O_2, and 98.5 vol.% helium. (▲) Pd/NAC1, (□) Pd/NAC2, (◆) Pd/NAC3, (△) Pd/NAC4, and (+) Pd/NAC5.

This harmful effect on conversion of methane can be attributed to excessive oxidation of palladium by the oxygen of ceria in the samples containing high amount of ceria. Also, encapsulation of metal active phases by ceria could occur due to high content of such rare earth in the support [26].

As can be seen, an adverse effect of higher ceria loading has been observed confirming the negative influence of this promoter in palladium-containing catalysts [6,7] in methane oxidation at low temperature even when incorporation of promoter to support was carried out by sol–gel method. Although samples with high ceria loading can be used as catalyst, it can be seen that high temperature is required in contrast with samples with low ceria loading; hence a formulation with low ceria loading apparently is the best solution for oxidation of methane. Although the catalyst with low ceria loading (Pd/NAC1) performs better than the others, samples containing 5, 10 and 15 wt.% of ceria allow for achieving 100% of methane conversion at temperature lower than 550 °C. In this study, the presence of carbon monoxide was not observed which could be attributed to the presence of ceria, in agreement with previous reports in the literature [6].

4. Conclusions

The effect of different ceria loading in CeO_2–Al_2O_3 and Pd/CeO_2–Al_2O_3 samples has been investigated through different characterization techniques and catalytic oxidation of methane at low temperature. Characterization techniques have shown that in catalytic samples with CeO_2 loading of 15 wt.% or lower the mixed support exhibits amorphous phases while high specific surface area is kept. The TPR profiles have evidenced the existence of oxygen absorbed in support and the presence of different cerium oxides and CeO_2 crystals whose reducibility is more difficult for samples with high ceria loading. Addition of precious metal enhances the reducibility of oxygen of ceria in samples with high ceria loading. Detrimental effect of high ceria loading in Pd/CeO_2–Al_2O_3 has been observed on catalytic oxidation of methane at low temperature under stoichiometric conditions, although the degree of depression of methane oxidation activity depends on ceria loading and particularly of cerium oxides present in the support, which can help to form particles of metallic palladium which are necessary for methane activation.

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