Methane oxidation behaviour over sol–gel derived Pd/Al$_2$O$_3$-ZrO$_2$ materials: Influence of the zirconium precursor

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ABSTRACT

This work constitutes an attempt to control the properties of palladium supported on alumina doped with zirconium used in methane oxidation. For this aim, two zirconium precursors were used and sol–gel method was adopted to prepare such catalysts. N$_2$ physisorption, XRD, scanning electron microscopy, H$_2$ chemisorption, H$_2$ TPR and NH$_3$ TPD are the main techniques used to characterize the catalysts. The use of different zirconium precursor affects significantly the textural and the structural properties of these materials. Furthermore, the catalytic activity is seen to depend on the zirconium precursor and the zirconium content simultaneously.

1. Introduction

Extensive research has been carried out on mesoporous materials because of their high potential as catalysts, adsorbents, electronic devices, and so on [1]. In terms of catalysis chemistry, they can provide us not only highly arranged catalyst sites on the surface where reactants are activated, but also the nano-sized space where the motion and conformation of the reactants should suffer strict constraints [2]. On the other hand, a particular interest has concerned the total methane oxidation because of the huge worldwide presence of natural gas and the fact that its combustion offers significant environmental advantages. Although natural gas combustion provides several advantages, the emission of unburned methane, which is the main component of natural gas, is a drawback given that methane is a potent greenhouse gas, which is recognized to contribute more, to global warming than CO$_2$ at equivalent emission rates [3]. Thus, numerous studies have been performed to totally oxidize methane. However, methane oxidation raises many difficulties. In fact, the high stability of the methane molecule together with the low temperatures at which the catalyst must operate (less than 500–550 °C) did not lead to an ideal catalyst which should exhibit the highest activity at the lowest temperature

and the best resistance to poisons present in the exhaust gases [4]. For all these reasons, many efforts have been performed to design catalytic materials that present good performances [5–8]. According to literature, two families of catalysts have been extensively studied during last decades. Among them, noble metal catalysts appeared as the best candidates [3]. Their properties in the complete oxidation of methane at low temperature were extensively studied so far. In particular, palladium and platinum based supported catalysts are recognized as the most active noble metals for the combustion of light alkanes [9–14]. The high volatility of the other noble metals makes them less attractive because of the high reaction temperatures reached during combustion. Furthermore, they can be obtained in a high degree of dispersion when deposited on conventional supports with a high specific area like silica or alumina [3]. Although supported palladium catalysts are usually prepared by impregnation of the support with Cl-containing metal precursors, sol–gel method seems to be more attractive to prepare these materials when deposited on binary oxides. The aim of this work is to prepare palladium supported on promoted alumina by adding zirconium. Two different zirconium precursors have been used. The first one is a zirconium alkoxide which is Zr(OC$_4$H$_9$)$_4$. This choice can be justified by the moderate reactivity of such alkoxide with water and because of the nature of the alcohol used as solvent during the preparation. The second Zr precursor used in this work is the zirconium acetylacetonate. According to a previous study already done in our laboratory, we have proved the benefit effect of the use of such zirconium precur-

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Table 1
BET surface area, average pore diameter D_p (Å), pore volume V_p (cm^3/g) and Pd dispersion (%D) of Pd-Zr$_x$-Al and Pd-Zr$_x$ (acac)-Al calcined at 500 °C.

Catalysts	S_{BET} (m^2/g)	D_p (Å)		V_p (cm^3/g)	Palladium dispersion (%)
		1st type	2nd type		
Pd/Al$_2$O$_3$	281	36	95	0.58	22
Pd-Zr$_2$-Al	245	36	92	0.54	05
Pd-Zr$_2$ (acac)-Al	297	–	79	0.84	05
Pd-Zr$_5$-Al	207	36	91	0.40	08
Pd-Zr$_5$ (acac)-Al	250	–	74	0.65	07
Pd-Zr$_{15}$-Al	127	35	73	0.10	10
Pd-Zr$_{15}$ (acac)-Al	175	–	80	0.49	24

sor when preparing mixed oxides [15]. Also, this precursor contains the acetylacetonate ligands known by their ability to interact with alkoxides.

2. Experimental

2.1. Catalysts preparation

Pd/Al$_2$O$_3$-ZrO$_2$ catalysts, with palladium loading of 0.5%, were prepared by following a sol–gel procedure. Palladium acetylace-toante (Acros, 34 wt. Pd%) and aluminium secondary butoxide (Acros 97%) are the precursors used to prepare palladium supported on alumina. The promotion of alumina with zirconium has been performed by using either the zirconium butylate Zr (OC$_4$H$_9$)$_4$ or the zirconium acetylacetonate Zr (C$_5$H$_7$O$_2$)$_4$. The preparation details are indicated below:

A mixture of aluminium s-butoxide (AsB) and s-butanol (sB) is stirred for 10 min, ([AsB] = 1 M), followed by the addition of the palladium acetylacetonate (Pd(acac)$_2$). The mixture is then kept for an appropriate time with constant stirring at 40 °C. Then, zirconium precursor is added to have a zirconium loading between 2 and 15 wt%. The hydrolysis step is assured by the addition of acetic acid (Scharlau, 99.8%) with a molar ratio n (CH$_3$COOH)/n (precursor) = 4. In fact, acetic acid could be used as a complexing agent and a water producer in situ due to the esterification reaction with the secondary butanol used as solvent. The obtained gel is dried in oven for 24 h and calcined in flowing oxygen (30 mL min^{-1}) at 500 °C for 2 h. The two obtained series were respectively designed by Pd-Zr$_x$-Al and Pd-Zr$_x$ (acac)-Al which may modify the interaction between the used precursors and thus the catalytic properties of palladium materials.

After being aged for 24 h, the obtained gels were oven dried in ordinary conditions at 70 °C to be finally calcined at 500 °C in flowing oxygen for 2 h. The two obtained series were respectively designed by Pd-Zr$_x$-Al and Pd-Zr$_x$ (acac)-Al.

Supports with zirconium loading of 15% were also prepared either with Zr(OC$_4$H$_9$)$_4$ or Zr(C$_5$H$_7$O$_2$)$_4$ using the same preparation procedure and the same hydrolysis agent (CH$_3$COOH).

2.2. Characterization techniques

Surface areas of samples were determined from the N$_2$ adsorption isotherms at 77 K with the BET method using a Micromeritics ASAP 2000 Analyzer. The samples were previously 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 $P/P_0 = 0.98$. Before the measurements, the samples were outgassed at 200 °C.

Catalysts morphology was observed by the scanning electronic microscopy technique using a FEI Quanta 200 apparatus coupled to EBSD detector.

XRD patterns were recorded on an automatic diffractometer (Philips Panalytical) using the Cu Kα radiation (λ = 1.54 Å) and a nickel monochromator.

Palladium dispersion was determined by the dynamic pulsed hydrogen chemisorption technique. Prior to the measurements, the sample was reduced in H$_2$ flow at 300 °C, and then evacuated under inert gas at 320 °C.

Acidity of support was determined by using NH$_3$ TPD technique. The temperature-programmed desorption (TPD) measurements were performed on an AutoChem II instrument (Micromeritics). A thermal conductivity detector 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 500 °C for 1 h in a flow of helium gas (40 mL min^{-1}) then cooled at 110 °C. Samples were then saturated with 10% ultrapure anhydrous ammonia gas (balance He, 50 mL min^{-1}) for 1 h and subsequently flushed with He (50 mL min^{-1}) at 110 °C for 2 h to remove the physisorbed ammonia. The heating rate for the TPD measurements, from 110 to 1000 °C, was 10 °C min^{-1}.

Temperature-programmed reduction of the catalysts was carried out in a stream of 5 vol% H$_2$ balanced with Ar at a flow rate of 30 mL min^{-1}. Prior to measurements, 50 mg of the sample was placed in a quartz tube heated for 1 h at 500 °C under an Ar stream, and then it was cooled to room temperature. After the stream was switched from Ar to reducing gas, the sample was heated by increasing the temperature linearly at a rate of 10 °C min^{-1}. The hydrogen concentration in the effluent was continuously monitored by a thermal conductivity detector.

2.3. Catalytic oxidation of methane

The catalytic tests were performed in a dynamic microreactor over the oxidized sample (100 mg). The gas mixture used comprised 1 vol% CH$_4$, 4 vol% O$_2$ and balance He and the gas flow was fixed at 100 mL min^{-1}. The effluent was analyzed on line by a gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak column.

These tests consisted of the evaluation of the activity of catalysts at 500 °C followed by a temperature-programmed reaction where the temperature was decreased with the purpose of quantifying the CH$_4$ to CO$_2$ oxidation capacity of the samples at low temperature.

We are practically interested in the determination of % methane conversion given as follow:

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

P_{CH_4} : partial methane pressure

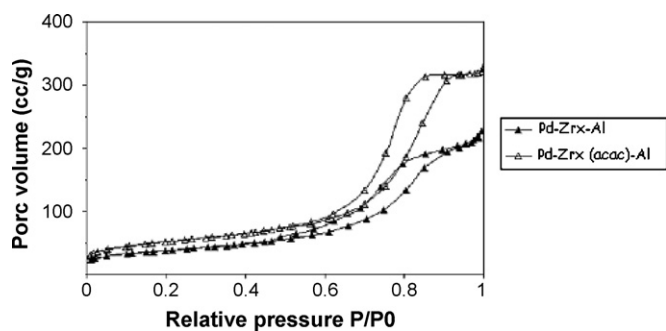P_{CH_2} : partial carbon dioxide pressure

Fig. 1. Effect of the nature of the zirconium precursor on the adsorption–desorption isotherm profile.

3. Results and discussion

3.1. Textural characterization

Table 1 compiles the BET surface areas and pore properties of all samples used in this study. As can be noted, the zirconium precursor affects significantly the textural properties of palladium materials. Although the two series of samples are mesoporous, two different hysteresis loops are obtained (see Fig. 1). Besides, as revealed in Table 1, samples prepared with $Zr(C_5H_7O_2)_4$ referred as Pd-Zr$_x$

(acac)-Al exhibit larger specific area and larger pore volume than that of Pd-Zr$_x$-Al. On the other hand, the increase of the zirconium loading has induced a decrease of the surface areas and the pore volume of all samples. According to previous work done by Schmal et al. [15], doping alumina with zirconium results in the blockage of some alumina pores by the zirconia crystallites. This observation could explain the surface area decrease observed in our case. Recent work interested in the exam of the properties of Pd/Al$_2$O$_3$-ZrO$_2$ prepared by impregnation [16] has also reported that the insertion of Zr^{4+} blocks the formation of Al–O–Al bond after drying and calcination, which may promote the formation of new pores and the decrease of the particle size and crystallization degree of Al$_2$O$_3$. This idea is in accordance with our results proved by the pore size decrease observed after the increase of the zirconium content. Here also, the zirconium precursor is seen to affect the decrease rate of the surface area of catalysts. In fact, compared to Pd/Al$_2$O$_3$ catalyst, a BET surface area loss of about 55% is observed on Pd-Zr$_{15}$-Al whereas only a loss of 35% is obtained for Pd-Zr$_{15}$ (acac)-Al.

The zirconium precursor is seen to also affect the pore distribution of catalysts. As shown in Fig. 2, using zirconium alkoxide led to two types of pores. Contrarily, homogeneous pore distribution was observed on catalysts prepared with the zirconium acetylacetonate. We also note the decrease of the number of pores with the zirconium content increase which may prove the idea already
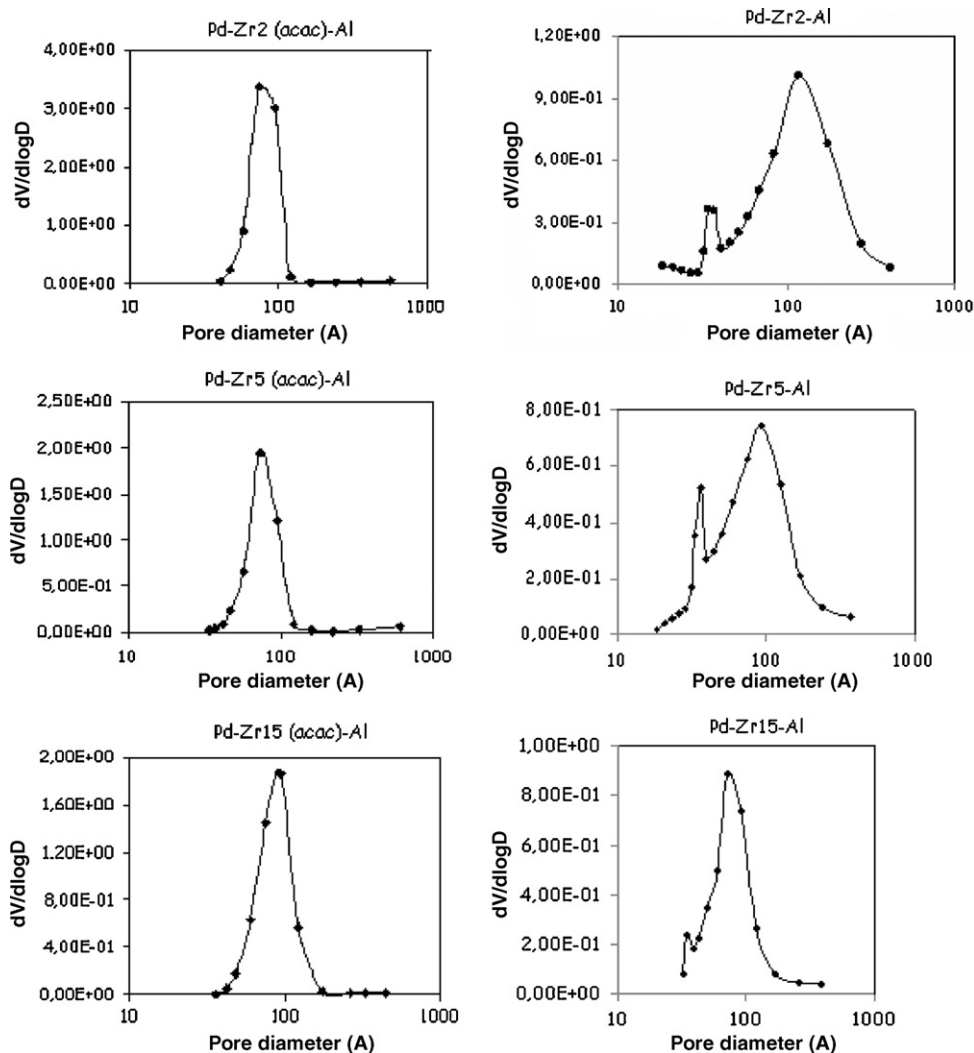

Fig. 2. BJH distribution profile of Pd-Zr$_x$ (acac)-Al and Pd-Zr$_x$-Al catalysts calcined at 500 °C.
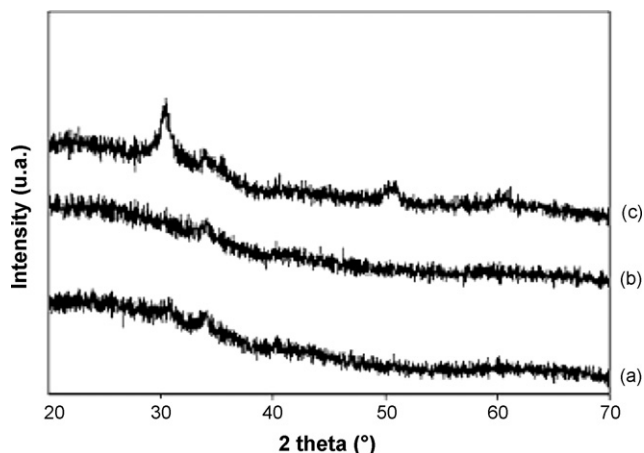
Fig. 3. XRD patterns of Pd-Zr$_x$-Al catalysts: (a) Pd-Zr$_2$-Al, (b) Pd-Zr$_5$-Al, (c) Pd-Zr$_{15}$-Al.

described about the blockage of the alumina pores by zirconia particles.

3.2. Crystalline phases

Figs. 3 and 4 illustrate, respectively, the diffraction patterns of Pd-Zr$_x$-Al and Pd-Zr$_x$ (acac)-Al samples. As expected, XRD analysis did not reveal the presence of peaks attributed to Pd or to its oxide for the two series of catalysts. This is understandable since the 0.5% concentration of Pd is below the detection limit of standard XRD. Besides, no alumina phase is observed. Similar results interested to the preparation of chromium oxide supported on alumina Cr/Al$_2$O$_3$ using the same precursors and the same drying mode, showed that alumina calcined at 500 °C exhibits an amorphous structure [17]. As presented in Fig. 3, the zirconium content increase leads to the appearance of peaks at about 30°, 50° and 60° characteristic of the tetragonal zirconia phase. This result predicts a decrease of the catalytic activity of Pd-Zr$_x$-Al at high zirconium content. In fact, this crystalline form of zirconia is reported to be less active than the monoclinic one in methane combustion [18]. Contrarily, Pd-Zr$_x$ (acac)-Al samples exhibit an amorphous structure even at high zirconium content. The results above show that ZrO$_2$ is highly dispersed on the alumina surface when using the acetylacetonate of zirconium as precursor. Furthermore, they could explain the substantial decrease of the specific surface area observed when the zirconium alkoxide is used as precursor.
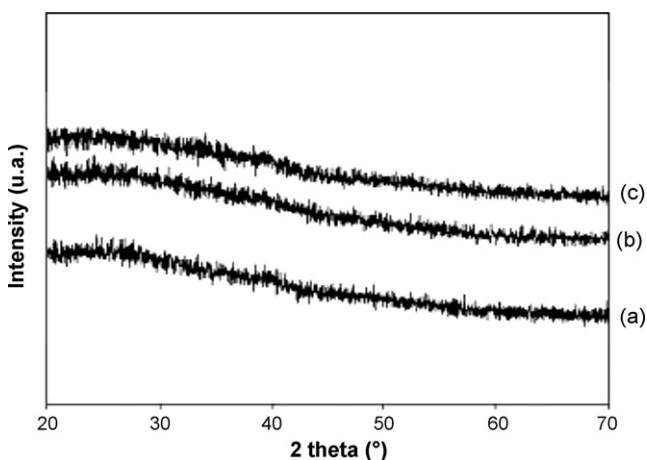

Fig. 4. XRD patterns of Pd-Zr$_x$ (acac)-Al catalysts: (a) Pd-Zr$_2$ (acac)-Al, (b) Pd-Zr$_5$ (acac)-Al, (c) Pd-Zr$_{15}$ (acac)-Al.

3.3. Catalysts morphology

Scanning electron microscopy was used to investigate the effect of the zirconium precursor on the morphology of catalysts. Only samples with Zr loading of 2% and 15% were characterized. At low zirconium content (Fig. 5a and c), the zirconium precursor affects a little the morphology of catalysts. However, as it can be seen, more homogeneous catalyst is obtained on zirconium rich catalyst when using acetylacetonate of zirconium (Fig. 5d). In fact, the Pd-Zr$_{15}$-Al image shows many types of particles whereas only one particle type is obtained on the Pd-Zr$_{15}$ (acac)-Al but with different sizes. However, it is difficult to know the origin of this homogeneity and may be further experiments should be done.

3.4. Palladium dispersion

The characterization of catalysts by H$_2$ chemisorption shows similar dispersion values at low zirconium content (see Table 1). In fact, for zirconium loading less than 5%, Pd/Al$_2$O$_3$-ZrO$_2$ catalysts exhibit similar palladium dispersion independently of the used precursor of Zr. This result could be justified by the same degree of homogeneity of the two kinds of catalysts. In fact, in our previous work [19], we have noted that the palladium dispersion depends on the catalyst homogeneity. More the catalyst is homogeneous, higher is the dispersion. This idea can be confirmed by the obtained palladium dispersions on zirconium rich samples. In fact, Pd-Zr$_{15}$ (acac)-Al dispersion is 2.5 greater than that observed on Pd-Zr$_{15}$-Al. These results could also be related to the acid/base properties of palladium support. In fact, Yoshida et al. [20] have noted that the palladium dispersions on the acidic supports were slightly smaller than basic ones. On the other hand, we have noted that the zirconium content increase leads to better palladium dispersion independently of the zirconium precursor. This behaviour could be explained by the decrease of the pores size and number caused by the blockage of the alumina pores. Thus, palladium particles could not penetrate into the support and still at the surface.

3.5. Supports acidity

It is established in the literature that ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts. Its strong basicity and smaller molecular size allows detection of acidic sites located in the narrow pores of the solids. For these reasons, we have used the ammonia TPD technique to determine the supports acidity. The obtained TPD profiles of Al$_2$O$_3$-ZrO$_2$ samples prepared with Zr(OC$_4$H$_9$)$_4$ or Zr(acac)$_4$ with zirconium loading of 15% are shown in Fig. 7. As can be noted, the two supports are found to be acidic. This result is in accordance with those of Dominguez et al. [21] who showed that Al$_2$O$_3$-ZrO$_2$ binary oxides prepared by sol–gel method exhibit an acidic behaviour and are active in the 2-propanol dehydration reaction. However, the zirconium precursor nature is seen to affect the nature of the acid sites. In fact, these sites are distributed in two temperature regions for support prepared with Zr (C$_5$H$_7$O$_2$)$_4$ (Fig. 6a). The first desorption maximum is observed at ~200 °C may be attributed to NH$_3$ chemisorbed on weak acid sites [22]. The second process starts slowly above 450 °C and becomes rapid at ~620 °C. This latter peak was observed on Al$_2$O$_3$-Zr$_{15}$ sample but with higher intensity. This desorption process or delay in NH$_3$ desorption indicates a stronger interaction of the acid sites with the adsorbed NH$_3$. It also indicates the unique presence of strong acid sites on support prepared with Zr(OC$_4$H$_9$)$_3$. In summary, we can say that support prepared with the zirconium alkoxide is more acidic than that prepared with the zirconium acetylacetonate. This result could explain the obtained palladium dispersion.
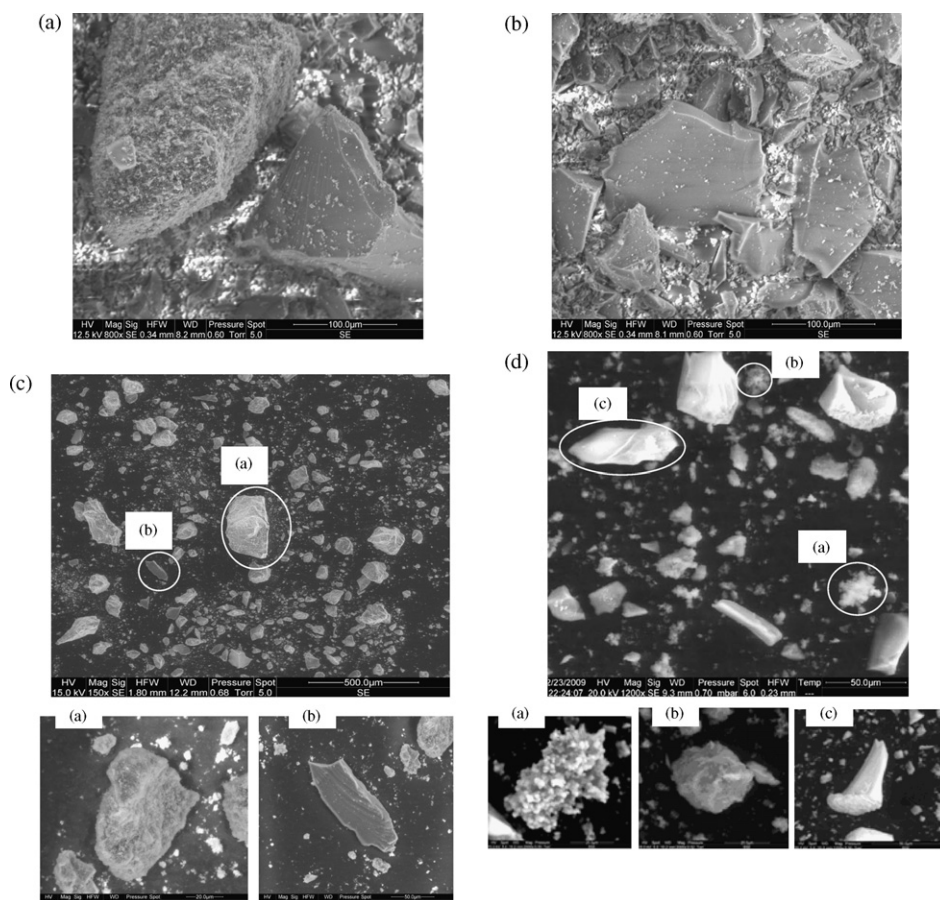
Fig. 5. SEM images of: (a) Pd-Zr$_2$ (acac)-Al, (b) Pd-Zr$_{15}$ (acac)-Al, (c) Pd-Zr$_2$-Al and (d) Pd-Zr$_{15}$-Al.

3.6. Palladium reducibility

H$_2$ TPR profiles of Pd/Al$_2$O$_3$-ZrO$_2$ samples are shown in Fig. 7. As it can be seen, a negative H$_2$-consumption peak occurs at 85 °C in all cases. According to literature, the presence of such peak is related to the decomposition of PdH$_x$ formed after the reduction of Pd at lower temperature. In fact, it is established that when hydrogen is passed over the supported Pd catalysts at room temperature, it is consumed rapidly. This suggests that the reduction of PdO formed on the supports could take place even before room temperature [23–25]. Noticeably, the evolution of hydrogen is accompanied by appreciable positive H$_2$-consumption peaks for Zr rich samples. This phenomenon indicates the occurrence of further reduction of PdO species which have not been reduced at room temperature. It is likely that smaller PdO particles, which interacted strongly with the metal oxide supports, are more resistive to reduction at low temperature [26]. Furthermore, the presence of such peak indicates a strong interaction between the palladium and its support and that
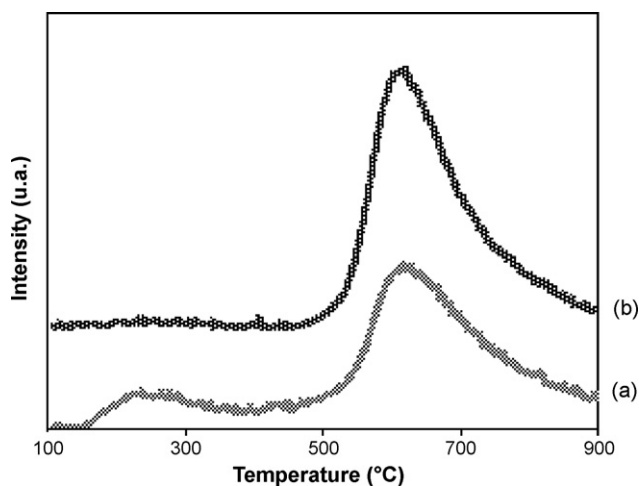

Fig. 6. TPD of ammonia over various Al$_2$O$_3$-ZrO$_2$ samples: (a) Al$_2$O$_3$-Zr$_{15}$ (acac) (b) Al$_2$O$_3$-Zr$_{15}$.
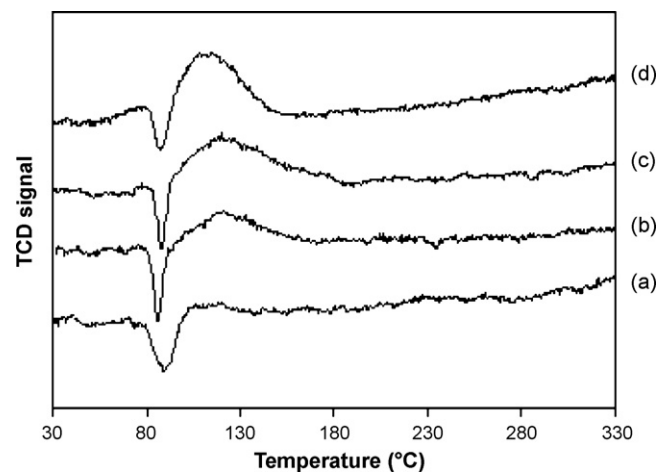
Fig. 7. TPR profile over Pd/Al$_2$O$_3$-ZrO$_2$ samples: (a) Pd-Zr$_2$ (acac)-Al (b) Pd-Zr$_2$-Al (c) Pd-Zr$_{15}$-Al and (d) Pd-Zr$_{15}$(acac)-Al.

Fig. 8. Effect of the zirconium loading on the activity of Pd-Zr$_x$ (acac)-Al.
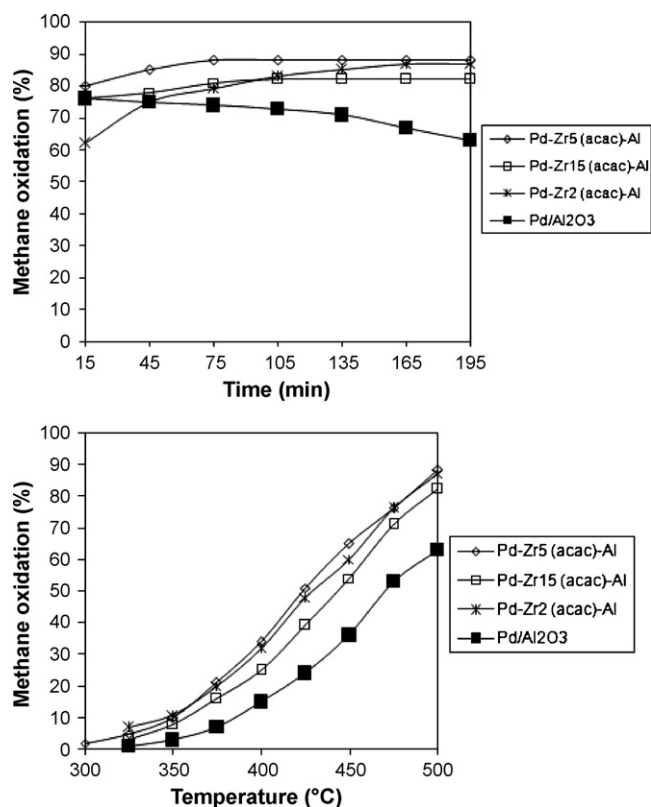

Fig. 9. Effect of the zirconium loading on the activity of Pd-Zr$_x$-Al catalysts.

this interaction is more accentuated for the catalyst prepared with Zr($C_5H_7O_2$)$_4$. This could be justified by the higher intensity of the peak on this catalyst.

3.7. Catalytic properties

The evolution of methane conversion over time shows the Pd/Al_2O_3 deactivation (Figs. 8 and 9). This deactivation is mainly due to the full oxidation of the palladium particles [27], to the poisoning effect of the formed water and carbon dioxide [28], or to the effect of formed carbonate species [29]. Conversely, all samples containing Zr exhibit activation during the first or the two first hours under reaction stream depending on the zirconium precursor (Figs. 8 and 9). The activity is then stabilized which could be justified by the higher oxygen mobility of ZrO_2 than that of Al_2O_3 [30]. In the same context, Ciuparu et al. [31] have reported that the rapid exchange of oxygen between ZrO_2 and oxygen in reaction gas can maintain PdO phase available during the methane combustion. Similarly, Guo et al. [15] interested in the investigation of the catalytic properties of Pd/Al_2O_3-ZrO_2 prepared by wet impregnation have shown that the presence of ZrO_2 can enhance the ability of providing active oxygen species which may be responsible of the stability of the activity over time.

On the other side, the nature of the zirconium precursor seems to affect significantly the catalytic behaviour of Pd/Al_2O_3-ZrO_2 materials. In fact, Pd-Zr$_x$ (acac)-Al samples have practically the same activity whereas a substantial decrease in the activity is observed for Pd-Zr$_x$-Al when the zirconium content is higher than 5%. This result is foreseeable because of the well-dispersed zirconia on alumina obtained on Pd-Zr$_x$ (acac)-Al. In fact, Souza et al. [32] have shown that Pt deposed ZrO_2 dispersed on high surface area support such as alumina were more active and stable than Pt/ZrO_2 and Pt/Al_2O_3 for autothermal reforming of methane. Furthermore, Sekizawa et al. [33] have reported that the increase in the amount
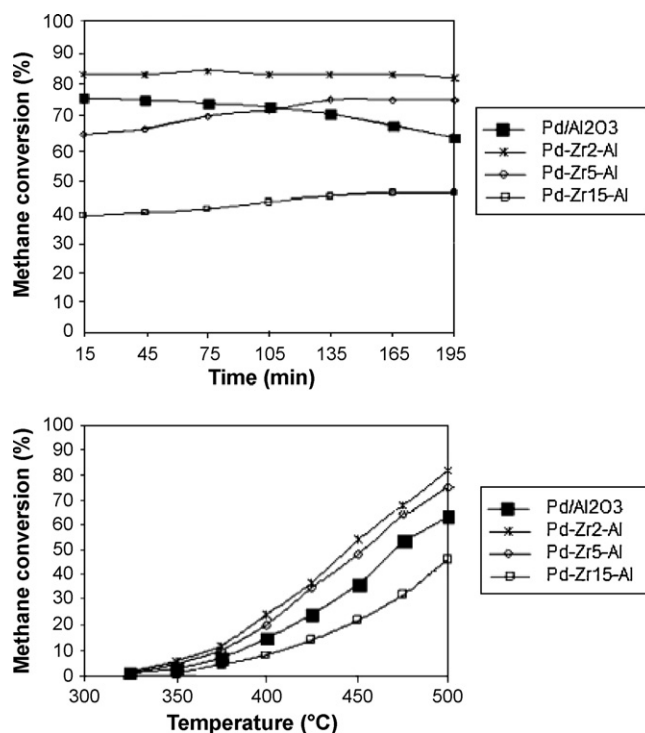
of zirconia tetragonal phase leads to lower activity which may explain the decrease of the activity when increasing the zirconium content for Pd-Zr$_x$-Al samples. On the other hand, and according to Souza et al. [34], zirconia is a reducible oxide and so the metal–oxide interaction can induce important modifications of the adsorptive and catalytic properties of the metal during reactions. Hence, it is reasonable to say that the modification of the zirconium precursor contributes to different metal–oxide interaction. The zirconium precursor could also affect the chemical state of palladium known as a key factor in the catalytic behaviour of palladium materials. In fact, some authors [36,37] proposed the acid/base or electrophilic/electrophobic property of both support and additives as a factor controlling the oxidation state of noble metals such as platinum and palladium, which in turn controls the catalytic activity of metal. Based on our results, we can say that the modification of the zirconium precursor plays a role in the chemical state of palladium. This hypothesis is in line with the XRD results. However, XPS should be used to confirm such idea.

Besides, the reducibility of palladium is known as a key factor of the catalytic behaviour of palladium materials. As it has been mentioned by Lin et al. [38], a catalyst with moderate reducibility and high oxygen exchange activity of PdO will have higher activity. Unfortunately, it is difficult to judge the reducibility of palladium in our case.

A comparison between our results and others already described in literature shows the benefit effect of the simultaneous use of alumina and zirconia. For instance, Pd/ZrO_2-MO_x materials (M = Co, Cr, Cu, Fe, Mn, and Ni) have been tested by Sekizawa et al. in total methane oxidation [35]. The catalytic activity of these materials was significantly retarded by the presence of metal oxides incorporated in the ZrO_2 support. Furthermore, based on the capability of ZrO_2 to interact with ceria, Pecchi et al. [39] have tried Pd/ZrO_2-CeO_2 system. However, these materials are totally inactive at 500 °C.

To conclude with these comparisons, cheaper catalyst containing a little quantity of Zr with high catalytic properties and more

developed textural properties can be obtained after mixing alumina with zirconia by sol–gel method.

In summary, the zirconium precursor plays an important role in the properties of palladium materials. It is clearly seen that the support acidity, hence the palladium dispersion depends on the zirconium source. Furthermore, at similar zirconium loading, the homogeneity of catalysts is more pronounced on catalysts prepared with Zr(acac)$_4$. Unfortunately, the origin of this homogeneity is not understood until now and needs further experiments. It is also interesting to note that the catalytic activity of Pd/Al$_2$O$_3$-ZrO$_2$ materials depends greatly on the zirconium precursor. According to the obtained results, Zr(acac)$_4$ appears as a good candidate to succeed the preparation of homogeneous matrices and to allow a good dispersion of palladium.

4. Conclusion

Pd/Al$_2$O$_3$-ZrO$_2$ materials prepared by following sol–gel procedure are seen to be active in methane oxidation. Catalysts with low zirconium content exhibit higher catalytic behaviour. Besides, the nature of the zirconium precursor seems to affect greatly the physic-chemical properties of Pd/Al$_2$O$_3$-ZrO$_2$. In fact, big differences were observed after the use of zirconium acetylacetonate as precursor. Amorphous structure reflecting the high dispersion of zirconia on alumina, accompanied by an enhancement of the textural properties was observed.

References

[1] J.Y. Ying, C.P. Mehnert, M.S. Wong, Angew. Chem. Int. Ed. 38 (1999) 56.
[2] T. Oikawa, Y. Masui, T. Tanaka, Y. Chujo, M. Onaka, J. Org. Chem. 692 (2007) 554.
[3] P. Gélin, M. Primet, Appl. Catal. B: Environ. 39 (2002) 1.
[4] P. Da Costa, R. Marques, S. Da Costa, Appl. Catal. B: Environ. 84 (2008) 214.
[5] R. Burch, P.K. Loader, Appl. Catal. B: Environ. 5 (1994) 149.
[6] K. Muto, N. Katada, M. Niwa, Appl. Catal. A 134 (1996) 203.
[7] A.F. Ahlstrôm-Silversand, C.U.I. Odenbrand, Appl. Catal. A 153 (1997) 157.
[8] J.C. Van Giezen, F.R. Van den Berg, J.L. Kleinen, A.J. Van Dillen, J.W. Geus, Catal. Today 47 (1999) 287.
[9] W.J. Kuper, M. Blaauw, F. Van Der Berg, G.H. Graaf, Catal. Today 47 (1999) 377.
[10] R. Prasad, L.A. Kennedy, E. Ruckenstein, Catal. Rev. Sci. Eng. 26 (1984).
[11] P. Briot, M. Primet, Appl. Catal. 68 (1991) 301.
[12] T.R. Baldwin, R. Burch, Appl. Catal. 66 (1990) 337.
[13] R. Burch, P.K. Loader, F.J. Urbano, Catal. Today 27 (1996) 243.
[14] G. Veser G, M. Ziauddin, L.D. Schmidt, Catal. Today 47 (1999) 219.
[15] L. Ben Hamouda, A. Ghorbel, J. Sol–Gel Sci. Technol. 26 (2003) 831.
[16] M. Schmal, M.M.V.M. Souza, D.A.G. Aranda, C.A.C. Perez, Stud. Surf. Sci. Catal. 132 (2001) 695.
[17] Y. Guo, G. Lu, Zh. Zhang, L. Jiang, X. Wang, Sh. Li, B. Zhang, J. Niu, Catal. Today 126 (2007) 441.
[18] F. Ayari, M. Mhamdi, G. Delahay, A. Ghorbel, Sol–Gel Sci. Technol. 49 (2009) 170.
[19] H. Alrai, H. Fukuzawa, Catal. Today 26 (1995) 217.
[20] C. Amairia, S. Fessi, A. Ghorbel, Sol–Gel Sci. Technol. 52 (2009) 260.
[21] Y. Yoshida, T. Nakajima, Y. Yazawa, T.T. Hattori, Appl. Catal. B: Environ. 71 (2007) 70.
[22] J.M. Dominguez, J.L. Hernandez, S. Sandoval, Appl. Catal. A 197 (2000) 119, 119.
[23] A. Corma, V. Fornes, M.I. Juan-Rajadell, J.M. Lopez Nieto, Appl. Catal. 116 (1994) 151.
[24] M.L. Cubeiro, J.L.G. Fierro, Appl. Catal. A 168 (1998) 307.
[25] N. Iwasa, N. Kudo, H. Takahashi, S. Masuda, N. Takazawa, Catal. Lett. 19 (1993) 211.
[26] Ch.T. Hong, Ch.T. Yeh, F.H. Yu, Appl. Catal. 48 (1989) 385.
[27] W.J. Shen, M. Okumura, Y. Matsumura, M. Haruta, Appl. Catal. A: Gen. 213 (2001) 225.
[28] H. Oh Se, P.J. Mitchell, R.M. Stiewert, J. Catal. 132 (1995) 287.
[29] R. Burch, F.J. Urbano, P.K. Loader, Appl. Catal. A 123 (1995) 173.
[30] S. Fessi, A. Ghorbel, A. Rives, R. Hubaut, Stud. Surf. Sci. Catal. 130 (2000) 3795.
[31] S. Yang, A. Maroto-Valiente, M. Benito-Gonzalez, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Appl. Catal. B 28 (2000) 223.
[32] D. Ciuparu D, E. Altman, L. Pfefferle, J. Catal. 203 (2001) 64.
[33] M.M.V.M. Souza, M. Schmal, Appl. Catal. A 281 (1–2) (2005) 19.
[34] M.M.V.M. Souza, D.A.G. Aranda, C.A.C. Pérez, M. Schmal, Phys. Status Solidi (a) 187 (2001) 297.
[35] K. Sekizawa, H. Widjaja, Sh. Maeda, Y. Ozawa, K. Eguchi, Catal. Today 59 (2000) 69.
[36] Y. Yazawa, H. Yoshida, N. Takagi, S. Komai, A. Satsuma, T. Hattori, J. Catal. 187 (1999) 15.
[37] Y. Yazawa, H. Yoshida, T. Hattori, Appl. Catal. A 237 (2002) 139.
[38] W. Lin, L. Lin, Y.X. Zhu, Y.C. Xie, K. Scheurell, E. Kemnitz, J. Mol. Catal. A 226 (2005) 263.
[39] G. Pecchi, P. Reyes, R. Zamora, T. Lopez, R. Gomez, J. Chem. Technol. Biotechnol. 80 (2005) 268.