Methane oxidation on Pd supported on high area zirconia catalysts

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Abstract

The results presented in this work clearly show that zirconia synthesized by precipitation of zirconyl chloride with NaOH leads to a zirconia with high surface area (224 m^2/g), which is relatively stable after high temperature exposure. Pd supported on this high surface area zirconia exhibit higher turnover frequency for methane combustion than when supported on zirconia obtained from zirconyl chloride precipitated with ammonium hydroxide.

We also found that when the commercial zirconium hydroxide is subjected to a NaOH reflux treatment, we obtained a zirconia of high and stable surface area (157 m^2/g) even after heating it at 700 °C. Pd supported on the Na treated commercially derived support shows the highest dispersion and the highest intrinsic activity than on any of the other preparations studied. The results presented in this paper open up a new venue for obtaining high surface area zirconia using the commercially available hydroxide.

This work shows that it is possible to stabilize zirconia using a Na treatment and also obtain high catalytic activity for methane oxidation on Pd stabilized on such support. Kinetic results and the corresponding mechanistic interpretation and the IR results support that the effect is consistent with increasing water support interactions which in term affect the reaction kinetics.

Keywords: Methane; Oxidation; Pd supported catalyst; High area zirconia

1. Introduction

The catalytic oxidation of methane has become the subject of several studies because of its potential application in power generation and for pollution control purposes in natural gas combustion [1]. Among the many catalysts studied for methane combustion, noble metals are more active than oxides [2–26], with Pd being the most active. Many materials have been studied as catalysts supports during this reaction, with alumina being the most common [3,5–14,20,23,24], followed by silica and other oxides [3,8,19]. The catalytic combustion of methane on Pd has also been studied on unsupported metallic monolith substrates [27]. In the last years, several papers have been published [5,13,15–18,21,25,26] on Pd supported on zirconia because it has been reported to be more active and stable than when supported on alumina [21]. Recently, Gelin and Primet [28] published a review on the catalytic combustion of methane on noble metals supported on different oxides. Choudhary et al. [29] also published recently an extensive review of the catalytic combustion of light hydrocarbons on oxides and supported noble metals.

A drawback of commercial zirconia is its low BET area, which is typically of the order of 50 m^2/g after calcination at 500 °C. Recently, however, several preparation methods to obtain high surface area zirconia have been reported in the literature. This includes, among others, impregnation of high surface area active carbon with zirconyl nitrate, addition of other oxides such as lanthanum oxide, magnesium oxide, calcium oxide, nickel oxide, aluminum oxide or yttrium oxide, and the addition of sulfuric acid to zirconia (see Chuah et al. [30] and references therein). In the case of sulfated zirconia, in addition of the thermal stability imparted by the sulfate group, it also generates acidity which makes these materials good acid catalysts for acid catalyzed reactions [31,32].

Recently, Chuah and Jaenicke [33] reported a method to prepare zirconia with high surface area and thermal stability using zirconium chloride and NaOH or KOH as precipitation agents. The resulting surface area depended on the precipitation

agent and the digestion time. While the specific area of the resulting zirconia hydroxide decreased with the digestion time, the stability to the subsequent thermal treatment reached a maximum at about 24 h of digestion. When NaOH was used as precipitation agent, the resulting area after calcination at 500 °C was about 250 m^2/g, decreasing to 170 m^2/g when calcining at 800 °C. The effect of NaOH in increasing the surface area was attributed by the authors to the "aggregation of particles during digestion followed by strengthening of the inter-particle contact" which diminishes sintering during calcination at high temperature. Chuah and Jaenicke [33] did not reported activity results of the effect of Na or other stabilizing methods such as the use of sulfated zirconia.

In this work we studied the oxidation of methane on Pd supported on the high area zirconia prepared with the method of Chuah and Jaenicke as well as the effect of the presence of sulfate groups on the surface on the activity. We also studied the effect of using NaOH to precipitate a commercially available zirconium hydroxide and obtained a high area zirconia. Pd supported on this material gave the highest activity of all the zirconia supports studied.

2. Experimental

2.1. Preparation of zirconia oxide supports

Three batches of the zirconia hydroxide were prepared. The first one by the conventional method using aqueous NH$_3$ as precipitating agent, the second one also using aqueous NH$_3$ as precipitating agent, but incorporating a reflux stage [34], and the third one by the method of Chuah and Jaenicke [33] using NaOH as precipitating agent.

In the conventional method, a solution of aqueous NH$_3$ is added drop by drop to 100 cm^3 of a 0.4 M solution of ZrOCl$_2$ (Merck) under continuous stirring until a pH of 10 is reached. The solution and resulting precipitate is left to age at room temperature for 24 h without agitation. The solid is filtered and washed with a solution of NH$_4$NO$_3$ to eliminate the Cl$^-$ ions until their presence in the washing solution is not detected by addition of AgNO$_3$. The resulting zirconium hydroxide, referred as ZH, is dried at room temperature for 24 h and then in an oven at 105 °C for an additional 24 h. The ZH powder is then calcined in air at 700 °C for 3 h heating at a rate of 1 °C/min. The resulting zirconia oxide thus obtained is referred as ZO.

The second batch is prepared in a similar way as the first one, but after the addition of NH$_4$OH, the resulting suspension is refluxed at 90 °C for 12 h as described by Chuah et al. [30]. The hydroxide precipitate is dried as described for the first method and it is referred as ZHr. A fraction of this zirconium hydroxide is calcined in air at 700 °C for 3 h, whereas the other fraction is sulfated and then calcined in the same way as the unsulfated zirconium hydroxide. The sulfidation of the ZHr hydroxide was carried out by adding to it 5 cm^3 of a 0.5 M H$_2$SO$_4$ solution per g of dry zirconium hydroxide by stirring the mixture for 1 h. The solid is then filtered and dried at 105 °C for 12 h. The zirconium oxide obtained using reflux followed by calcination

is referred as ZO$_{rf}$, whereas the one obtained after sulfating is referred as SZO.

The third batch of zirconia hydroxide is obtained using NaOH as the precipitation agent following the procedure reported by Chuah and Jaenicke [33]. In this case 100 cm^3 of the 0.4 M ZrOCl$_2$ solution are added slowly under agitation to 30 cm^3 of a 5 M solution of NaOH. The solution is refluxed for 12 h and then is filtered and washed as previously described and then dried at 105 °C for 12 h. The resulting Na containing hydroxide, referred as ZHNa, is separated into two fractions. The first fraction is calcined at 700 °C for 3 h, to obtain a solid referred as ZONa. The second part of the ZHNa is washed with NH$_4$NO$_3$ to reduce the amount of Na$^+$ using a method similar to that reported by Chin et al. [35] with zeolites. The ZHNa powder is contacted with a 2.25 M solution of NH$_4$NO$_3$ and boiled under a reflux for 2 h. The solution is filtered and washed with distilled water. This procedure is repeated three times and the resulting solid is dried at 105 °C for 12 h and calcined at 700 °C for 3 h to yield a solid that is referred as ZONa-w.

2.2. Pd impregnation of the zirconia supports

The five zirconia supports (ZO, ZO$_{rf}$, SZO, ZONa and ZONa-w) were impregnated with an aqueous solution of Pd(NO$_3$)$_2$ (Merck) containing the amount of Pd required to obtain a 1% loading of Pd, using the incipient wetness method. The impregnated supports were dried in air at room temperature for 8 h and then at 105 °C for 12 h. Previous to activity measurements the catalysts are calcined in-situ at 500 °C for 1 h.

2.3. Characterization

The surface area (BET) and pore size distribution of the various zirconia oxide powders prepared were obtained from N$_2$ adsorption isotherms using a Micromeritics 2010 adsorption apparatus. Previous to the adsorption measurements all the samples were degassed in vacuum at 200 °C. The crystal structure was determined by a Siemens D-5000 diffractometer using a Cu Kα radiation and a scan rate of 0.02°/min. The Na content of the ZONa and ZONa-w supports was determined by ICP using a Perkin-Elmer P-400 ICP-OES apparatus.

The Pd dispersion was measured by H$_2$ chemisorption before and after reaction according to the procedure described by Maffucci et al. [36] using the "*pulse method*" in a flow continuous apparatus. Previous to the chemisorption measurements the fresh catalyst is first calcined in-situ in air at 500 °C followed by reduction in a stream of 5% H$_2$/Ar at 300 °C for one hour. To measure the dispersion in the catalyst after reaction, the used catalyst is transferred to the chemisorption apparatus, then calcined in-situ at 300 °C for 1 h, and then reduced in the same way as described for the fresh catalyst.

2.4. Activity measurements

Catalysts' activity was measured in a flow tubular quartz reactor of 1 cm i.d. and 50 cm long, using 0.2 g of catalyst that

occupies a bed length of about 0.2 cm. The flow rates are kept constant by electronic mass flow controllers, and a temperature controller using a feedback from a thermocouple placed in a thermo-well located in the center of the catalyst bed controls the reactor temperature. All the runs were made at atmospheric pressure.

Prior to each run, the catalyst is calcined in-situ at 500 °C in a stream of pure oxygen flowing at 10 cm^3/min for 1 h followed by cooling to 50 °C in oxygen. At this point the reaction mixture is added until a total flow of 100 cm^3/min is reached having a composition of methane of 1.5% and 6.0% oxygen with He as balance. Temperature programmed reaction (TPR) experiments were conducted by increasing continuously and linearly the reactor temperature at 2 °C/min until reaching 500 °C. In a different type of experiment, when the activity is measured as a function of time-on-stream (TOS), the temperature was increased *stepwise* maintaining it constant for a period of time, typically 3 h. Two centimetres of the reactor effluent is sampled on line and injected into two gas chromatographs (GC-Perking Elmer Autosystem) equipped with thermal conductivity detectors. The first GC is equipped with a HAYESEP D column (Alltech) of 1.8 m long maintained at 34 °C in a He flow of 20 cm^3/min, which separates CH_4 from CO_2. The second GC is equipped with a Molecular Sieve 5A (Alltech) column 100 cm long maintained at 34 °C in a He flow of 20 cm^3/min to separate O_2 and CO. Both these measurements are used to calculate the methane and oxygen conversion as well as CO and CO_2 production. As no CO formation was observed in any of the runs, conversion was directly related to CO_2 formation.

For each activity measurement, a new sample of the fresh catalysts is charged in the reactor. In TPR experiments, the reactor effluent is sampled at equal time intervals corresponding to various temperatures. During time-on-stream (TOS) experiments, in some cases at a given constant temperature, the conversion initially increased with time-on-stream and then it reached a constant value. This increase in conversion with time is referred hereafter as "activation".

2.5. DRIFTS measurements

The IR measurements were obtained in a Fourier Transform Infrared Spectrometer (Bruker, Equinox 55). The DRIFTS reaction cell has ZnSe windows and a praying mantis optical geometry (Harricks, 3-3S). The cell includes a heating element and a thermocouple, which provides the feedback to a temperature controller (Omega, CN8200 Series) to maintain the temperature constant at a set value. The gases flow in under the catalyst holder, through the bed and out of the base of the cell. Due to the high gas phase volume at the dome of the cell supporting the windows, it is necessary to purge CO with He first to be able to measure the signal corresponding to adsorbed CO. Infrared spectra were recorded in Kubelka–Munk units and over the range of 4000–500 cm^{-1} at 250 scan rate and 4 cm^{-1} of resolution. A dilution ratio of KBr:catalyst of 10:1 was used for every sample. In every run 50 mg of sample were reduced in 50 cm^3/min of H_2 at 200 °C for 2 h. Then the sample was cooled down to room temperature in flowing He and the background was taken. CO was introduced at room temperature by flowing 50 cm^3/min of a mixture of 5% CO in He for 30 min. Then He was introduced to purge CO and spectra of the adsorbed species were obtained. Then the temperature was increased at 1 °C/min and the procedure was repeated at different temperatures.

3. Results and discussion

3.1. Characterization of the zirconia supports

The results of the physical and chemical characterization of the zirconia supports are summarized in Table 1. Zirconia hydroxide prepared by the conventional method (ZH) using NH_4OH as precipitant has a relatively high surface area of 350 m^2/g *before calcination*. The area of the resulting oxide (ZO), however, is drastically reduced to 27.7 m^2/g *after calcination* at 700 °C. The zirconium hydroxide obtained using NH_4OH as precipitant but adding a reflux (ZHr) has the same area as the one obtained by the conventional method and is not included in Table 1. However, and in agreement with the literature [30,33], the zirconia obtained after calcination of this hydroxide has a BET area of 74.8 m^2/g which is almost twice the value obtained by the conventional method without reflux. XRD results of the resulting ZO powders (not shown) exhibit diffraction lines corresponding to the monoclinic phase only.

Calcining the *sulfated* hydroxide results in a solid with a surface area of 101.7 m^2/g (SZO) confirming the well known stabilizing effect of the sulfate groups [37]. XRD results show

Table 1
Physical characterization of zirconium hydroxides and the zirconia supports

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (Å)	XRD crystalline phase[a]	% Na
ZH	350.1	0.30	37.2	–	–
ZO	27.7	0.13	149.1	m	–
ZO$_{rf}$	74.8	0.26	114.6	t	–
SZO	101.7	0.22	68.4	t	–
ZHNa	358.9	0.55	50.6	–	–
ZONa	224.3	0.306	44.0	t	0.47
ZONa-w	232.8	0.326	43.6	t	0.09

[a] m: monoclinic; t: tetragonal.

that the predominant crystal phase in SZO is the tetragonal phase instead of the monoclinic phase of ZO.

When the precipitating agent is NaOH, the resulting hydroxide (ZHNa) has a BET area of 358.9 m^2/g, similar to the one obtained by the conventional preparation. After calcination at 700 °C, however, the resulting oxide (ZONa) has a BET area of 224.3 m^2/g, which is almost an order of magnitude higher than that of the oxide obtained in the absence of Na ions. Standard analysis of XRD results at low resolution show a single broad peak at 30° that appears to be the tetragonal phase instead of the monoclinic phase of ZO. Further work is underway to study this peak at high resolution to determine if there is a contribution from the cubic phase. The surface area, the Na content of 0.45%, and the XRD results showing mainly the tetragonal phase are in agreement to those reported by Chuah and Jaenicke [33], confirming the significant stabilizing effect of the presence of Na.

The washing procedure used to decrease the Na content of the ZHNa zirconium hydroxide was effective in reducing the Na concentration in ZONa from 0.47 to 0.09% in the ZONa-w zirconium oxide, while keeping a high surface area of 232.8 m^2/g. XRD patterns obtained after washing show that the crystalline phase remains unchanged as the tetragonal phase.

3.2. Characterization of the Pd phase

Pd dispersion results from hydrogen chemisorption assuming H/Pd = 1 are listed in Table 2. Pd dispersion measured after reaction (and pretreatment) were similar to those before reaction suggesting that in this case for experiments below 700 °C, no significant changes occurred during reaction. It can be seen that there is no clear correlation between Pd dispersion and the zirconia support surface area. In the unsulfated zirconia supports (ZO and ZO$_{rf}$) the dispersion is practically the same (37–38%) even though the BET area or the ZO$_{rf}$ is about twice that of ZO (28 versus 75 m^2/g). Likewise the dispersion is slightly higher in the ZONa-w support (43%) even though its BET area is the highest (232 m^2/g). The highest dispersion (56.3%) is obtained on the support prepared using NaOH as precipitant (ZONa) and the lowest on the support that was sulfated (SZO). Materials with higher BET area and the same Na loading exhibit lower Pd dispersion suggesting the Na surface area might not be the main factor affecting dispersion. This factor cannot be ruled out, however, because the area of exposed Na and acidity of the zirconia supports was not

measured since the focus was on stabilizing zirconia and not optimizing Pd dispersion. In studies of NO reduction with CH$_4$, Chin et al. [35] proposed that sulfated zirconia stabilizes Pd^{+2} or PdO in a highly dispersed form, accordingly, one would expect a higher dispersion on this catalyst contrary to our results. One cause for the low H$_2$ uptake observed might be the presence of S species on Pd surface which would translate into low dispersion.

4. DRIFTS results

CO adsorption was carried out on the pre-reduced catalysts shown in Fig. 1. In the case of Pd/SZ, Fig. 1C, shows bands characteristic of sulfated zirconia at 1329 cm^{-1} attributed to S=O stretching [50,52] and a band at 1204 cm^{-1} assigned to S–O [48,51]. All the catalysts show a band at 1630 cm^{-1} assigned to adsorbed molecular water on the support [48,53,54], which in the case of Pd/SZ gradually desorbs when increasing temperature. This does not occur for Pd/ZONa-w and Pd/ZONa, for which this band increases with temperature, and even at 200 °C this peak still remains, evidencing a strong interaction of water with the supports. This could be an indication that the basicity of the surface due to the presence of sodium promotes the adsorption of weakly adsorbed molecular water.

All the samples exhibit a typical broad band around 3600–3000 cm^{-1} corresponding to weakly H-bonded surface hydroxyls bonded to the support [48]. In the samples containing sodium, Fig. 1B and D, a small sharp peak appears around 3740 cm^{-1} as temperature increases, which has been assigned to terminal singly coordinated OH groups on the support [48,49,68]. This group has been attributed an important role on the activity of tetragonal sulfated zirconia when studied on *n*-butane isomerization as a probe reaction [69]. This peak is only weakly observed on Pd/SZ at 25 °C and disappears when further increasing temperature. In the case of the tetragonal Pd/ZONa-w and Pd/ZONa, both samples show this peak.

The peak around 1960 cm^{-1} has been previously reported as corresponding to bridge bonded CO over reduced Pd(1 1 0) [5,12,55,58,59] and it is seen on Pd/ZrO$_2$, Fig. 1A, and with low intensity on Pd/SZ, Fig. 1C, in both cases, decreasing as temperature increases. Interestingly, both samples containing sodium do not exhibit this band at any temperature.

All catalysts exhibit a band around 1850 cm^{-1}, which has been assigned to multicoordinated CO bonding on reduced palladium [54,56,57]. In the case of Pd/ZrO$_2$, it is shifted to

Table 2
Pd dispersion, temperature for 50% of methane conversion (T_{50}), effective pre-exponential factor (A_{eff}) and apparent activation energy (E_{app}), and turn over frequency (TOF) at 342 °C (k_{eff} at X_{CH_4} = 33%)

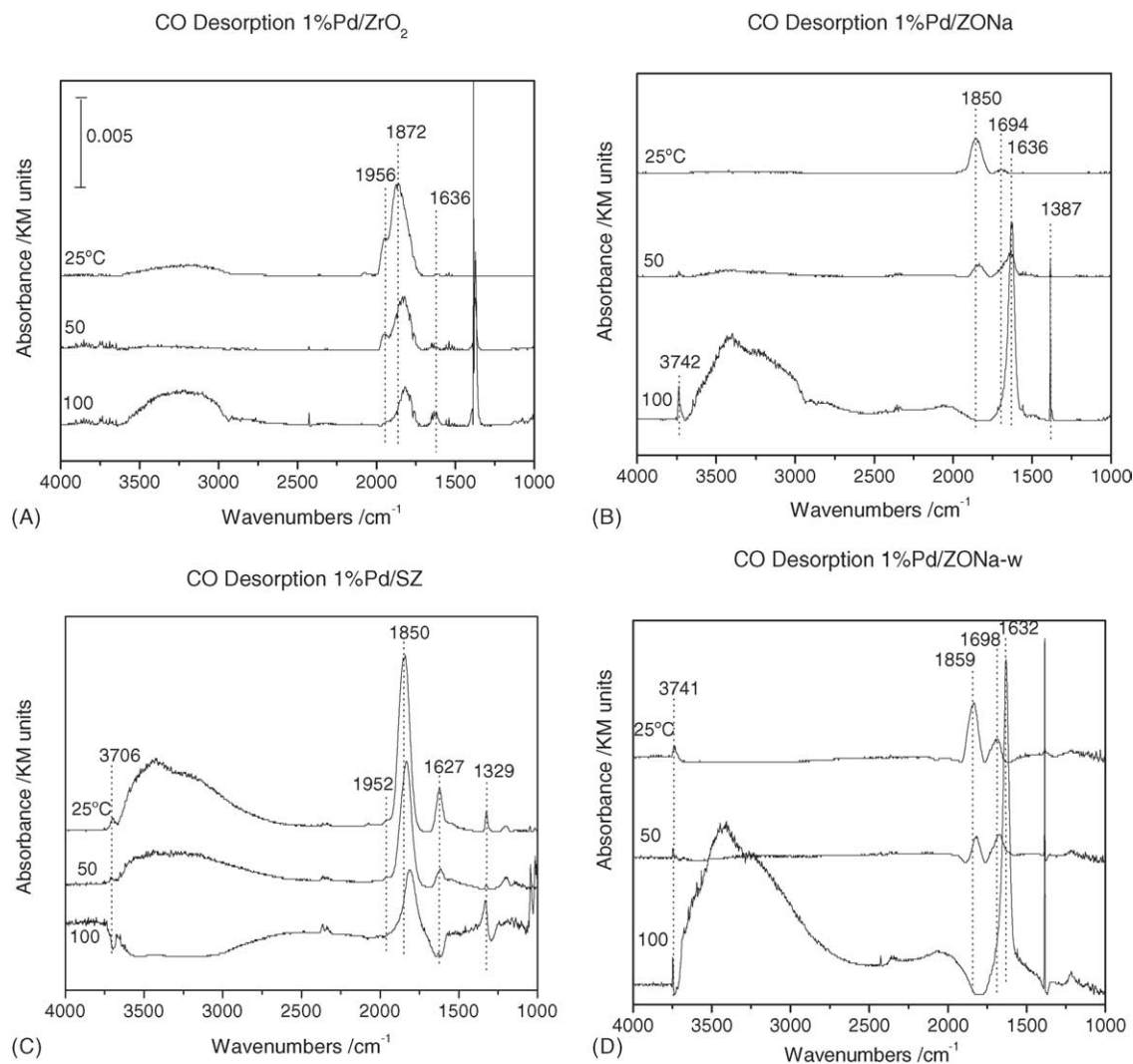| Catalyst	Dispersion fresh catalyst (%)	T_{50} °C	A_{eff} (mol CO$_2$/mol exposed Pd s)	E_{app} (kcal/mol)	TOF (mol CO$_2$/mol exposed Pd s)
Pd/ZO	37.5	371	1.3×10^{13}	42.4	0.011
Pd/ZO$_{rf}$	38.7	371	0.9×10^{13}	42.1	0.009
Pd/SZO	28.1	356	4.6×10^{19}	60.2	0.018
Pd/ZONa	56.3	343	3.4×10^{17}	53.7	0.028
Pd/ZONa-w	42.9	342	1.9×10^{16}	50.5	0.021

Fig. 1. Diffuse reflectance FTIR for CO desorption on: (A) 1%Pd/ZrO₂; (B) 1%Pd/ZONa; (C) 1%Pd/SZ; and (D) 1%Pd/ZONa-w. Each spectrum is labeled with its corresponding temperature. All the samples were reduced at 200 °C in hydrogen before proceeding to the CO adsorption, and then the temperature ramp was carried out in flowing He at 1 °C/min.

1872 cm^{-1} evidencing a strong CO–metal interaction. This multibonded CO species gradually desorbs as temperature increases, and in the case of Pd/ZONa-w and Pd/ZONa, this absorption band completely disappears around 100 °C. This behavior could be explained in terms of the presence of sodium, which promotes the formation of palladium–CO–alkali species [53,57,59–61], decreasing the strong CO metal interaction. It should be noticed that the desorption of CO is accompanied by the appearance of a strong peak at 1387 cm^{-1} possibly due to the formation of carbonates on the support [54,57,62]. This is not observed on the Pd/SZ catalyst.

5. Activity results

TPR experiments with the supports without Pd showed conversions below 1% at 450 °C except for the ZONa support, which showed about 6% conversion at 450 °C. This is in contrast with results reported by Epling and Hoflund [21] who report that zirconia has its own activity for methane combustion. We would like to point out, however, that in experiments with an older blank reactor (no catalysts), wherein some high temperature calcination of noble metal containing catalysts had been conducted, methane oxidation activity was observed. We repeated the experiments with a new blank reactor and found no activity from the reactor walls. Hence, we are certain that the zirconia supports without Pd exhibit no significant activity for methane combustion at $T < 400$ °C.

The conversion versus temperature results during a TPR experiment for Pd supported on pure zirconia supports (ZO and ZO$_{rf}$), free of Na and S, are presented in Fig. 2. These catalysts have similar Pd dispersions but different BET areas and give very similar conversions. These results further confirm that the zirconia supports have no activity for this reaction in agreement with the results obtained on zirconia without Pd. If zirconia had activity, then the zirconia-supported catalysts with the highest area, ZO$_{rf}$, would have shown higher conversion since their Pd dispersion (i.e. its active area) are similar.
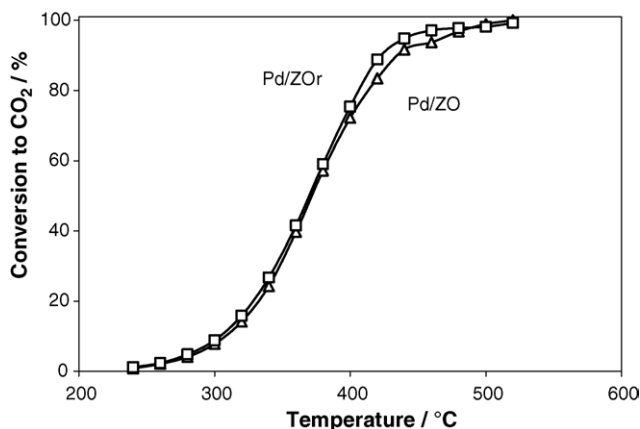
Fig. 2. CH$_4$ to CO$_2$ conversion during TPR experiments for 1%Pd/ZO and 1%Pd/ZO$_{rf}$ catalysts. Temperature ramp rate: 2 °C/min; total flow rate: 100 cm^3/min of a mixture of 1.5% CH$_4$, 6.0% O$_2$, balanced in He; mass of catalyst loaded: 0.2 g.

Fig. 3A–D show the conversion versus temperature results obtained on catalysts supported on ZO$_{rf}$, SZO, ZONa and ZONa-w, respectively. These results were obtained using two heating protocols: a continuous TPR ramp (curve (a)) and a stepwise temperature increase (curve (b)). The results show that in all cases the conversion from curve (b) (i.e. stepwise ramp) is higher than when using a continuous ramp during TPR experiments. Since in the stepwise experiments the conversion is measured after 2–3 h of time-on-stream, it is clear that the

catalyst undergo some activation after equilibration with the reactants. No such activation is evident during the continuous TPR ramp experiments because there is no sufficient time for equilibration. Pd supported on unmodified zirconia (Pd/ZO$_{rf}$) show a slight increase in activity with time-on-stream at temperatures above 370 °C, whereas Pd/ZONa-w shows the highest increase followed by Pd/ZONa and Pd/SZO. Such increases in activity during the first 3 h of reaction have also been reported by Ribeiro et al. [13] for a 10% Pd/ZrO$_2$ catalyst, whereas other authors [21] have reported stable conversions. Garbowsky et al. [12] attributed the activation of Pd/Al$_2$O$_3$ to structural changes from Pd(1 1 1) to Pd(2 0 0) occurring in the presence of the reactive mixture that facilitates the change from oxidized Pd to reduced Pd. Yang et al. [23] have shown that during reaction, the Pd surface of a Pd/ZrO$_2$ catalyst undergoes a transformation to a very active phase consisting of Pd/PdO$_x$. On the other hand, Roth et al. [38] have shown that elimination of Cl$^-$ ions in catalysts prepared using chlorinated precursors can explain the reports of activation occurring during reaction. Similar findings have been reported by Gracia et al. [39] during oxidation reactions on Pt supported on alumina and silica during CO and ethane oxidation but not during methane oxidation since the latter reaction requires higher temperatures on Pt. These authors also reported that the effect of Cl depended on the reaction conditions and the support used.

Although we used a Cl-free Pd precursor to prepare our catalysts, traces of Cl from the Zr oxychloride precursor used
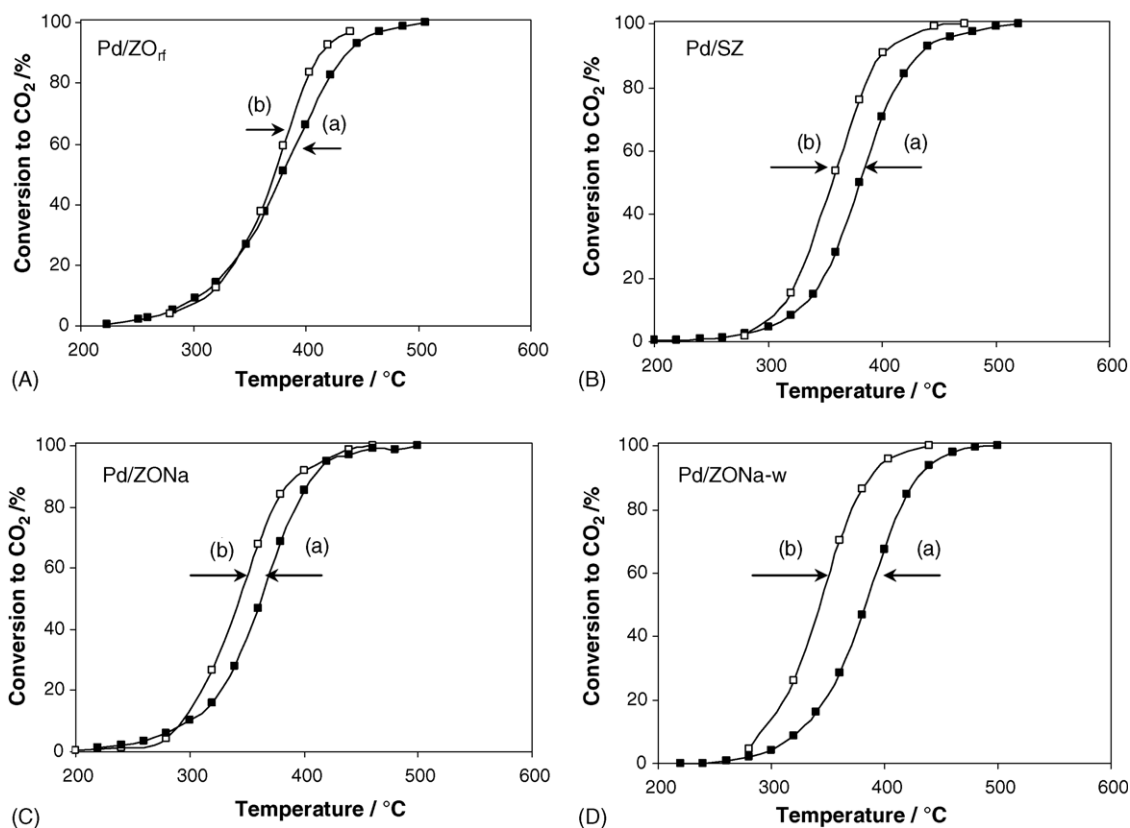

Fig. 3. CH$_4$ to CO$_2$ conversion vs. temperature for the various 1%Pd catalysts. (A) Pd/ZO$_{rf}$; (B) Pd/SZ; (C) Pd/ZONa; and (D) Pd/ZONa-w. Curve (a): TPR with constant temperature ramp rate of 2 °C/min; curve (b): keeping temperature constant until a stable conversion is attained at each temperature. Temperature ramp rate: 2 °C/min; total flow rate 100 cm^3/min of a mixture of 1.5% CH$_4$, 6.0% O$_2$, balanced in He; mass of catalyst loaded: 0.2 g.

in the preparation of the zirconium hydroxide could be present even though care was taken to ensure the elimination of Cl. However, the highest increase in conversion with time-on-stream is observed on the Pd/ZONa-w catalyst that has been subjected to treatments that facilitates the elimination of the residual Cl (three refluxes with NH_4NO_3). Thus, it is unlikely that Cl is the cause of activation during time-on-stream. Instead, the oxidation state of the Pd surface, which is determined by the reaction environment, is the most likely cause of this effect as shown by recent results by Wolf and coworkers using in-situ IR [40].

When the conversions after 3 h (form curves (b) in Fig. 3) are compared, Pd supported on the Na treated zirconia (Pd/ZONa and Pd/ZONa-w) exhibits the highest TOF followed by Pd/SZO and by the least active Pd/ZO$_{rf}$. This can be seen in Table 2 (third column), which shows the temperature corresponding to 50% conversion (or light off temperature, LOT). The LOT decreases as the activity (rate per g of Pd loaded) of the catalyst increases. To rationalize these results the reaction rates in terms of kinetic parameters are compared.

It has been reported that the reaction rate during methane combustion on Pd supported on alumina and zirconia is inhibited by H_2O and CO_2 [13,25,39,41–43]. At low CO_2 concentrations, Au-Yeung et al. [22] proposed that the rate of methane combustion on Pd/ZrO_2 could be approximated by the following kinetic expression:

$$R_{CO_2} = k_{eff} \frac{[CH_4]}{[H_2O]} \tag{1}$$

where k_{eff} [mol of CO_2/(mol Pd s)] is the experimental effective rate constant for CO_2 formation and $[CH_4]/[H_2O]$ is the ratio of the methane and H_2O gas phase concentration, respectively. Assuming a plug–flow reactor behavior, integration of Eq. (1) leads to the expression:

$$k_{eff} = \frac{2F_{CH_4}}{n_s} [-\ln(1 - x) - x] \tag{2}$$

where F_{CH_4} is the methane inlet flow rate, n_s the number of surface Pd atoms (obtained from the dispersion results) and X the fractional conversion of methane to CO_2.

Table 2 summarizes the kinetic parameters obtained for the various catalysts in terms of an effective pre-exponential factor A_{eff} and the apparent activation energy E_{app} obtained from:

$$k_{eff} = A_{eff} \, e^{-E_{app}/RT} \tag{3}$$

These parameters were obtained in the 260–340 °C temperature range and from the constant steady state conversion values for each temperature obtained using the stepwise method (curves (b) of Fig. 2). For the Pd/ZO catalysts we used the conversion values from Fig. 2 because in the range of temperatures used, this catalyst does not undergo activation. In all cases, we obtained good linearity between experimental results and Eq. (3) with a correlation coefficient of 0.99 or higher.

As it can be seen in Table 2, Pd supported on ZO and ZO$_{rf}$ have very similar kinetic parameters with an apparent activation energy of about 42 kcal/mol, which is similar to the values reported in the literature [22,42]. This also shows the self-consistency and reproducibility of our results. It should be noted that if water inhibition is not accounted for, i.e. the reaction is assumed to be zero order with respect to water partial pressure, the apparent activation energy becomes 21 kcal/mol. This value is similar to values reported for PdO supported on ZrO_2 and Al_2O_3 under dry conditions (see [25] and references cited therein).

The catalysts prepared over the sulfated zirconia show a significant increase in the activation energy to a value of 60 kcal/mol and at the same time an increase in the pre-exponential value of several orders of magnitude, relative to Pd supported on ZrO_2. This occurs because the rates per g of catalyst are similar and since the activation energy increases, the calculated pre-exponential factor must also increase to yield comparable rates. The increase in the activation energy due to the presence of sulfur is expected and has been reported by others. Lampert et al. [44], reported an increase of 7 kcal/mol in the activation energy for methane total oxidation on catalysts supported on Pd/ZrO_2-SiO_2 and Pd/Al_2O_3 after exposure to 0.9 ppm of S at 325 °C during times varying from 4 to 13 h. The increase in the activation energy is attributed by Lampert et al. to the formation of low activity sites such as PdO/SO$_x$. It is possible that a similar effect due to S migration from sulfated zirconia to Pd can occur in this catalyst leading to an increase in the activation energy. The cause of the increase in the effective pre-exponential factor however is less obvious since several factors are lumped to determine the value of this parameter.

The Na containing catalysts also exhibit an increase in the activation energy and in the pre-exponential factor, but less pronounced than on the sulfated zirconia support. These rather abnormal kinetic parameters indicate that the structural changes caused by the effect of Na on ZrO_2 has also an indirect effect on the active phase of Pd when compared with those obtained on Pd supported on untreated ZrO_2.

An explanation to the values of the kinetic parameters obtained on the Na treated zirconia and sulfated zirconia can be proposed from considerations of the effect of water on the reaction. Kikuchi et al. [45], assumed that the rate determining step is the adsorption of methane, as it has been proposed in the literature [25], and proposed that the rate of reaction can be expressed by:

$$R_{CO_2} = k_r[CH_4]\theta_v \tag{4}$$

where θ_v is the fraction of empty sites. Considering that water adsorption is at equilibrium and that the coverage of other species is negligible, Kikuchi proposed that:

$$\theta_v = \frac{1}{1 + K_{H_2O}[H_2O]} \tag{5}$$

where K_{H_2O} is the adsorption equilibrium of water on Pd. Substituting Eq. (5) onto (4) we obtain:

$$R_{CO_2} = \frac{k_r[CH_4]}{1 + K_{H_2O}[H_2O]} \qquad (6)$$

which becomes Eq. (1) when $K_{H_2O}[H_2O] \gg 1$. Under such conditions $k_{eff} = k_r/K_{H_2O}$, therefore the enthalpy for water adsorption on Pd becomes incorporated in the apparent activation energy, and the equilibrium constant into the effective pre-exponential factor. Using Eq. (6) as the starting point of their analysis, Kikuchi et al. developed experiments to evaluate these parameters on Pd supported on Al_2O_3, SnO_2 and Al_2O_3-NiO. These authors found that the enthalpy for water adsorption as well as the activation energy for the reaction (Eq. (3)) depended on the support. Thus, the support can affect indirectly the effective kinetic parameters by affecting the adsorption of water on the Pd active phase. In the case of the Na treated zirconia, if we assume that Na is not affecting directly the Pd surface, then the above analysis implies that the adsorption of water on the support is affecting the water adsorption on Pd. The high area of Na treated zirconia might facilitate the spillover of water from the Pd to the support thus decreasing the value of adsorbed water on Pd and increasing the value of A_{eff}. This is consistent with the IR results (Fig. 1), which show that the sodium containing catalysts have a strong capacity to stabilize water on the support. While changes in the activation energy suggest a change in the reaction mechanism, the IR results point out that such change can result from water interaction, which affect the enthalpy of water adsorption. This can account for the change in activation energy as previously discussed.

The Pd/PdO_x surface ratio is another factor that can be affected by the treatment of the sulfated and Na treated zirconia supports [12,23]. The effect of alkalis in supported palladium catalysts by transferring electron density to the metal is well known [57]. If this ratio determines the active phase, then the high area of the Na treated zirconia can alter this ratio and change both the apparent activation energy and the effective pre-exponential factor.

While the effective kinetic parameters change significantly with the zirconia treatment, the turnover frequency (or TOF) at 342 °C, only changes by a factor of 3 as shown in Table 2. The rates were calculated at 33% conversion because in the equation for a plug flow reactor with a first order reaction (Eq. (1)) the conversion in the reactor cancel out and the rate equals the rate

constant. The LOT listed in Table 2, show that the most active catalysts (Pd/ZONa and Pd/ZONa-w) also have the lowest LOT and the higher TOF (~ 0.02 s^{-1}).

To study the effect of high temperature exposure in the activity, the TPR experiments were conducted on fresh catalysts samples, but the temperature was programmed to reach 700 °C and maintained at this value for 1 h in the reaction mixture. The catalysts were then cooled down to 500 °C in He, calcined again at that temperature for 1 h, and then cooled to room temperature. A TPR experiment was then conducted from room temperature to 550 °C. The conversion versus temperature observed during the TPR experiment and the steady-state conversion obtained using the stepwise temperature increase are shown in Fig. 4, curves (a) and (b), respectively. It can be seen that after the high temperature treatment the catalysts again exhibit similar activation than the fresh samples (Fig. 3) when the two conversions are compared. As it is the case in the catalysts not pretreated at 700 °C, the extent of activation is slight for the $PdZO_{rf}$ catalysts but it is pronounced for the Pd/ZONa-w catalysts. These results further support our conclusion that the activation is not linked to the presence of Cl since these catalysts have been subjected to high temperature (700 °C) in the reaction mixture. This would result in the elimination of Cl [38], yet the activation process is similar to the observations in the fresh catalysts calcined only at 500 °C.

Pd dispersions at room temperature after the treatment at 700 °C are shown in Table 3. As expected, in all cases there is a decrease in dispersion after heating in the reaction mixture. Nonetheless, the catalysts precipitated using NaOH, which have the highest dispersion and BET area before heating, still retain high dispersions. Furthermore, after heating at 700 °C, these catalysts (Pd/ZONa, Pd/ZONa-w) also have the highest activity and thus lowest LOT, as shown in Table 3. After heating at 700 °C, however, the Pd/SZO has now a lower activity with a LOT similar to Pd/ZO$_{rf}$. The BET areas after the pretreatment (not shown) are similar to those obtained before heating, indicating that no significant textural changes occurred in the support.

The kinetic parameters after heating at 700 °C, also shown in Table 3, indicate that those of Pd/ZO$_{rf}$ remain about the same. The activation energies of the other catalysts decrease by about 3–4 kcal/mol, whereas the pre-exponential factors decrease by an order of magnitude. The values of the kinetic parameters rank in about the same order as the catalysts not exposed to high temperature listed in Table 2. The TOF at 342 °C reported in the last column of Table 3 shows that, except for the Pd/SZO catalyst, the other catalysts have TOF of the same order of

Table 3
Pd dispersion, temperature for 50% of methane conversion (T_{50}), effective pre-exponential factor (A_{eff}) and apparent activation energy (E_{app}), and turn over frequency (TOF) at 342 °C, after exposing the catalysts to the reactive mixture at 700 °C for 1 h (k_{eff} at X_{CH_4} = 33%)

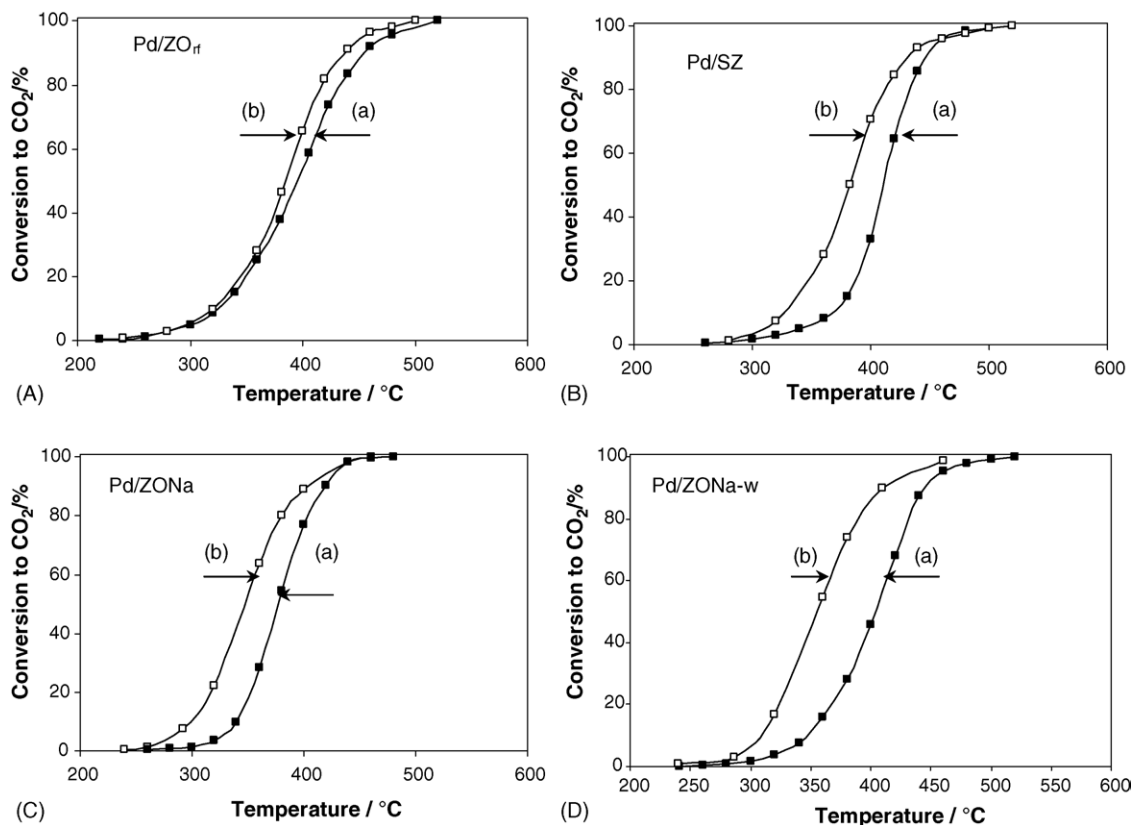| Catalyst	Dispersion (%)	T_{50} °C	A_{eff} (mol CO_2/mol exposed Pd s)	E_{app} (kcal/mol)	TOF (mol CO_2/mol exposed Pd s)
Pd/ZO$_{rf}$	13.5	384	1.1×10^{13}	41.8	0.015
Pd/SZO	17.5	382	1.1×10^{18}	56.8	0.007
Pd/ZONa	31.6	347	2.9×10^{16}	50.3	0.038
Pd/ZONa-w	33.0	355	1.8×10^{15}	47.6	0.022

Fig. 4. CH$_4$ to CO$_2$ conversion during TPR experiments for the various 1%Pd catalysts after treatment at 700 °C for 1 h in reaction mixture. (A) Pd/ZO$_{rf}$; (B) Pd/SZ; (C) Pd/ZONa; and (D) Pd/ZONa/w. Curve (a): TPR with constant temperature ramp rate of 2 °C/min; curve (b): keeping temperature constant until a stable conversion is attained at each temperature. Temperature ramp rate: 2 °C/min; total flow rate 100 cm^3/min of a mixture of 1.5% CH$_4$, 6.0% O$_2$, balance He; mass of catalyst loaded: 0.2 g.

magnitude before and after heating at 700 °C. The decrease in the TOF of the Pd/SZO catalyst is consistent with the S poisoning effect of the active sites proposed by Lampert et al. [44], which is favored by the higher temperature and the presence of water. The water generated by the reaction mixture favors the spillover of SO$_x$ species from the support into the Pd surface, which explain the decrease in the effective pre-exponential factor with respect to the values before heating at 700 °C [46].

The good activity results obtained with the zirconium oxide stabilized with Na lead us to use this treatment on the commercial hydroxide, provided by the MEL company, by refluxing it with NaOH for 12 h, followed by overnight drying in air at 105 °C. The solid is then washed with a solution of ammonium nitrate, as in the case of the Pd/ZONa-w, dried at 105 °C and then calcined at 700 °C for 3 h. The treated MEL hydroxide, as well as the untreated sample, were impregnated with 1% Pd in the same way as described for the other catalysts,

and are referred as Pd/ZONa-w (MEL) and Pd/ZO (MEL). The textural characteristics of these catalysts are listed in Table 4. It can be seen that the calcined commercial sample has an area of about 36 m^2/g, whereas the NaOH treated commercial sample has a significant higher area of 157 m^2/g after heating at 700 °C for 3 h. This is quite interesting because it shows that the commercial hydroxide can be treated with NaOH to yield a zirconia with high area after high temperature calcination. The crystal phase of the stabilized Pd/ZONa-w (MEL) sample appears to be tetragonal. Moreover, the Pd dispersion on both calcined samples, with low and high BET area, is relatively high on both samples confirming that the dispersion is not related to the BET area.

Methane conversion results for the catalysts prepared from the MEL precursor using the stepwise heating are shown in Fig. 5. The TPR results (not shown) exhibit the same trend as those prepared in the ZO$_{rf}$ and ZONa-w supports, i.e. a slight activation for the catalysts without the Na treatment, whereas

Table 4
Characterization and kinetics parameters of catalysts prepared over commercial zirconium oxide MEL (with and without treatment with NaOH)

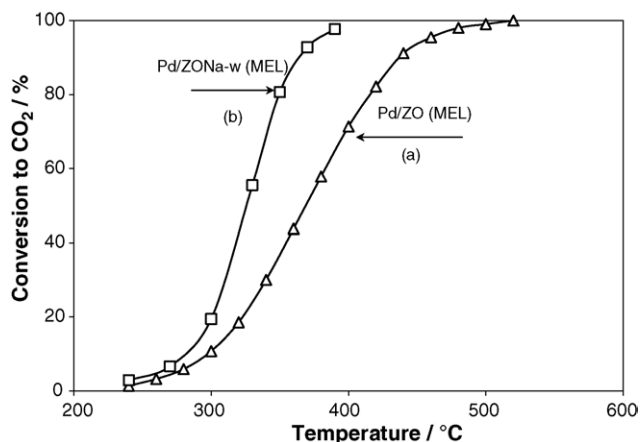| Catalyst	BET area (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (Å)	Dispersion (%)	T_{50} °C	A_{eff} (mol CO$_2$/mol exposed Pd s)	E_{app} (kcal/mol)	TOF (mol CO$_2$/mol exposed Pd s)
Pd/ZO (MEL)	36.2	0.093	76.6	62.4	370	1.1×10^{12}	39.5	0.010
Pd/ZONa-w (MEL)	157.1	0.316	54.2	76.0	325	4.7×10^{16}	50.2	0.068

Fig. 5. Comparison of stable CH_4 to CO_2 conversion of 1%Pd catalysts supported over commercial zirconium oxide provided by MEL. Curve (a): Pd/ZO (MEL), obtained by Pd impregnation of zirconium hydroxide MEL previously calcined at 700 °C for 3 h; curve (b): Pd/ZONa-w (MEL), obtained by impregnation of zirconium hydroxide MEL previously treated with NaOH, and calcined at 700 °C for 3 h. Temperature ramp rate: 2 °C/min; total flow rate 100 cm^3/min of a mixture of 1.5% CH_4, 6.0% O_2, balanced in He; mass of catalyst loaded: 0.2 g.

there is a strong activation for the Na treated catalysts. As it can be seen in Fig. 5, the Na treated sample is more active than the untreated sample and in fact the LOT is the lowest than any of the previous catalysts synthesized from zirconium oxychlorides. It is important to note that the Cl content of the commercial zirconia is only 0.02% so the increased activity of the Pd/ZONa-w (MEL) catalyst cannot be attributed to elimination of Cl due to the NaOH treatment. Roth et al. [38] reports that no inhibition effect was detected in their studies of Pd/Al$_2$O$_3$ catalysts having Cl concentrations of 0.015%. The effect of NaOH treatment on the catalysts prepared from the MEL hydroxide is similar to the effect on Pd/ZO and Pd/ZONa-w. There is an increase of both the apparent activation energy to a value around 50 kcal/mol, and an increase in the pre-exponential factor of about 3–4 orders of magnitude. The TOF however is about three times higher and the LOT (325 °C) is the lowest one obtained in this study. The higher TOF can be partially explained by the highest dispersion. The TOF does not seem to be affected by Pd dispersion but we cannot conclude definitively that the reaction is structure insensitive. Other factors such as oxygen diffusion, the Pd/PdO$_x$ ratio, and water migration on the support can also play a role in the activity results obtained. It is clear that the Na treatment has a significant effect in Pd supported on either supports but the intrinsic activity is the highest on the MEL treated support. The common factor among the more active catalysts is the higher area of the supports. The kinetic analysis presented suggests that the effect of water on the support is one of the possible causes that explain why the specific activity of Pd is affected by the various supports and their treatments. The presence of sodium seems to favor water migration to the support. This could be due to or result from the progressive change in the Pd/PdO$_x$ ratio. The nature of the activation of the catalysts with time-on-stream (Figs. 3 and 4) is still unresolved but we think that oxygen diffusion through the support could

play an important role and this process increases when sodium is present in the support. It is well known that oxygen can diffuse through the bulk of zirconia [47,63], which is facilitated by the formation of vacancies created by the incorporation of cations [64]. The oxygen species would react with CO to produce adsorbed CO_2 and carbonates. The same phenomenon has been observed in Ce-Zr mixed oxides under CO pulses [65–67], where oxygen diffusion plays a fundamental role. This diffusion process is not observed when the bare zirconia has not been doped by cations [64]. Further work is underway to determine the nature of the zirconia phase using high resolution XRD under reaction conditions to resolve a possible contribution of the cubic phase in the Na treated catalysts. A change in crystal phase could lead to a change in the defect structure of the support, and this can certainly contribute to a change in the adsorptive properties of the support that can affect indirectly the reaction kinetics.

6. Conclusions

The results presented in this work clearly show that the synthesis procedure described by Chuah and Jaenicke lead to a support that results in a very active supported Pd catalyst for methane oxidation. The precipitation of the zirconyl chloride with NaOH leads to a zirconia with high surface area, which is relatively stable to high temperature exposure. This translates in a higher intrinsic activity of Pd for methane combustion.

We also found that when the commercial zirconium hydroxide is subjected to a NaOH reflux treatment we obtained a zirconia of high and stable surface area. Pd supported on the zirconia obtained from the Na treated commercial zirconium hydroxide shows high dispersion and the highest intrinsic activity. This opens up a new venue for obtaining high surface area zirconia using the commercially available hydroxide. We speculate that the Na effect on the activity is due to the decrease in the water coverage on Pd due spillover and absorption on the high area zirconia support obtained with the Na treatment.

Acknowledgements

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