

Methane combustion over Pd/SiO₂ catalysts with different degrees of hydrophobicity

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Abstract

The combustion of methane has been studied over 1% Pd catalysts supported on commercial silica with different hydrophobicity, prepared by chlorine free precursors. It was found that, when no water is added to the feed, the degree of hydrophobicity of the silica does not affect significantly the behavior of the catalysts. The results show that the activation and deactivation processes are similar for both catalysts. Furthermore, contrary to what is observed on Pd/Al₂O₃ and Pd/ZrO₂ catalysts, the apparent reaction order with respect to water for Pd/SiO₂ catalysts is -0.25 . When water is added to the feed, however, the different hydrophobicity of the supports affects the inhibition produced by the adsorption of water on the catalytic surface. Regardless of the hydrophobicity of the support, the addition of water also speeds up the deactivation process of the Pd catalysts supported on silica.

Keywords: Methane combustion; Supported Pd catalyst; Silica; Zirconia; Water inhibition

1. Introduction

The catalytic combustion of methane is a subject of great interest for energy production with low NO emission as well as for the elimination of traces of CH₄ that has not been combusted in devices that use natural gas as fuel [1]. Recently, Gelin and Primet [2] published a review that summarizes the knowledge about the catalytic combustion of methane on noble metals. Almost at the same time, Choudhary et al. [3] published a review on the oxidation of light hydrocarbons, which also includes, beside the noble metals, other types of catalytic systems.

The highest activity for methane combustion under lean conditions (excess of O₂) has been shown to occur on supported Pd [4–10]. The supports most commonly used are alumina [8,9,11–36] and zirconium oxide [8,19,29,30,32,35,37–43]. Studies of methane oxidation over Pd/Al₂O₃ catalysts show that the activity of the catalysts is not constant in time. Activation with time during

exposure to the reacting mixture has been reported by several authors [9,11,14,18,19,20,25,29,30,33]. After the initial activation period a decrease of the catalytic activity is observed with time [25,29–34]. Various researchers have proposed that structural changes of the catalytic surface may explain the initial activation of the Pd/Al₂O₃ catalysts [13,18,32]. Without discarding this explanation, Roth et al. [33] showed clearly that in the cases where either a Cl-containing precursor is used or the support contains Cl, the activation may be explained by the gradual elimination of that species. In addition, various explanations for the deactivation of Pd/Al₂O₃ catalysts with exposure to the reacting mixture have been proposed in the literature. While Muto et al. [25] correlate the loss of activity with the sintering of Pd particles, Roth et al. [33] suggest that the deactivation can be explained by the formation of low activity species, Pd(OH)₂, on the surface of the Pd oxide. The formation of Pd(OH)₂ species has also been suggested by other authors [4,19,21]. In contrast with Pd catalysts supported on Al₂O₃, Pd catalysts supported on ZrO₂ show a stable activity over time [29,30]. This is the reason why there is a growing interest in studying the Pd/ZrO₂ catalysts.

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The presence of water as a reaction product or added into the feed, decreases the activity of Pd/Al₂O₃ [7,19,21,28] and Pd/ZrO₂ [35,39,42] catalysts during methane combustion. In the case of Pd supported on alumina and zirconium oxide, an order close to -1 with respect to H₂O has been determined at temperatures below 500 °C. The inhibition process may occur by the competitive adsorption of H₂O on the surface of the PdO, therefore decreasing the number of active sites for methane adsorption. Considering the inhibiting effect of water, it has been suggested that the hydrophobicity of the support may have an important role in the activity of the supported Pd catalysts. Thus, Nomura et al. [29] propose that the difference in affinity for water adsorption of alumina and zirconium oxide would explain the deactivation showed by Pd/Al₂O₃ catalysts with time of exposure under the reacting mixture, while the Pd/ZrO₂ catalysts show a constant activity with time.

Although silica is a traditional catalyst support, the number of papers published on the combustion of methane over the Pd/SiO₂ system is more limited. Some important differences with respect to Pd supported on alumina have been reported. Baldwin and Burch [12] found that the activation of Pd/SiO₂ in the presence of the reacting mixture is much faster than in Pd/Al₂O₃. Hoyos et al. [17] found that, while the activity of Pd/Al₂O₃ catalysts increases notably by treatment with the reactive mixture at 600 °C, the activity of Pd/SiO₂ catalysts remains practically constant. A study of the effect of the reaction products, H₂O and CO₂, in the activity of Pd catalysts supported on alumina and silica was made by Burch et al. [21]. These authors found that water inhibits the activity of both catalysts, but the effect of the presence of CO₂ is greater on Pd/SiO₂ catalysts. The reaction order with respect to water for the Pd/SiO₂ catalyst, however, was not reported in that work. Additionally, Muto et al. [25] have shown that the Pd/SiO₂ catalysts are rapidly deactivated in the presence of the reacting mixture, and proposed that the deactivation is related to a decrease of the catalyst dispersion. However, these authors point out that the initial activity of Pd/SiO₂ is much greater than that of Pd supported on alumina. The reason for the different behavior of catalysts supported on alumina or silica is not clear. Burch [44] has suggested that the capacity of the support to adsorb water can affect the catalyst's activity by its influence on the partial pressure of the water in the neighborhood of the active surface of the Pd oxide particles.

This work presents the study of the effect of water at low (dry feed) and high concentration (wet feed) during methane combustion over Pd/SiO₂ catalysts. In particular, the influence of the support's hydrophobicity in the catalytic behavior of the system is also investigated, in order to find out a possible relationship between the water adsorption capacity and the deactivation process of the catalyst. The kinetics data for the Pd/SiO₂ catalysts are compared with those obtained with a Pd/ZrO₂ catalyst under identical experimental conditions.

2. Experimental

Several catalysts with a nominal 1% Pd content were prepared using ZrO₂ synthesized in our laboratory as support, and two types of commercial silica with different degrees of hydrophobicity and similar specific surface area: a hydrophilic silica, Aerosil 130, and a methoxylated hydrophobic silica, R972, both from Degussa®. The zirconium oxide was obtained by precipitation of zirconium oxychloride with a solution of ammonium hydroxide using the method described by Risch and Wolf [45]. The zirconium hydroxide thus obtained was dried in an oven at 105 °C for 12 h, and then calcined in a muffle furnace at 700 °C for 3 h, to yield zirconium oxide. Pd was impregnated on the ZrO₂ and the Aerosil 130 support using an aqueous solution of Pd(NO₃)₂ (Merck). In the case of the R972 hydrophobic silica the precursor was Palladium acetyl acetonate Pd(C₅H₇O₂)₂ dissolved in acetone. In all cases the impregnation was carried out using a slight excess of the precursor solution, and evaporating to dryness. The impregnated supports were then dried in an oven at 105 °C during 12 h.

The BET specific surface area of the different supports and catalysts was determined in a Micromeritics ASAP 2010 apparatus by physical adsorption of nitrogen. The dispersion for the different catalysts in the reduced state was determined in a continuous chemisorption apparatus by titration of the chemisorbed oxygen with hydrogen at 150 °C, according to the method described by Maffucci et al. [46]. Reduction of the catalysts was achieved using a 20 cm³ min⁻¹ flow of a mixture of 5% H₂/Ar at 300 °C for 1 h. The nomenclature and description of the catalysts, as well as the specific BET area data and dispersion of the catalysts are given in Table 1.

To determine the catalytic activity, 0.2 g of catalyst were loaded into a 50 cm long and 1 cm diameter tubular reactor. The catalyst was calcined in situ during 1 h at the required temperature (500 °C for the Pd/ZO and Pd/A 130 catalysts, and 400 °C for the Pd/R972 catalyst) in a 10 cm³ min⁻¹ stream of pure O₂, and cooled in O₂ to room temperature. Then the reactants were allowed to flow (90 cm³ min⁻¹) at a concentration of 1.5% CH₄ and 6.0% O₂, balance He. The temperature was increased at 3 °C min⁻¹ using an RKC model REX-P100 programmer, from room temperature to the desired reaction temperature. The effluent from the reactor was analyzed by gas chromatography using two Perkin-Elmer Autosystem chromatographs equipped with HWD detectors. The first chromatograph had a HAYASEP D

Table 1
Nomenclature and characterization of the catalysts

Nomenclature	Support	BET area (m ² g ⁻¹)	Dispersion (%)
Pd/ZO	Zirconium oxide	28	46.8
Pd/A130	Aerosil 130	137	31.7
Pd/R972	Aerosil R972	145	30.1

(2 m × 1/8 in.) column to analyze CH₄ and CO₂, and the second one had an MS 5A (1 m × 1/8 in.) column to analyze O₂ and CO.

Some experiments were also made adding water to the feed. Thus, once the catalyst reached a constant activity in the “dry” stream, the feed was directed to a bubbler containing water at a constant temperature of 24 °C and from there into the reactor. After analyzing the effluent from the reactor every 20–30 min over a period of 2 h with the catalyst being exposed to the “wet” feed, the gas flow was returned to its initial course and the conversion was again determined under a “dry” feed.

Changes in the hydrophobicity of the methylated Aerosil R972 support after preparing the catalyst or after reaction were checked by IR analysis of the methyl and hydroxyl groups found on the surface of the support. These experiments were carried out using an IR reactor cell (ISRI), equipped with temperature control and gas inlet and outlet to control the atmosphere within the cell. Samples of the fresh support or the used catalyst were pressed at 15,000 psi to form a transparent wafer that was placed in the sample holder of the IR cell. The cell was then placed in the chamber of a Bruker model Vector 22 spectrometer, and purged by He at 150 °C to eliminate moisture. The IR spectrum of the solid was obtained using air as background, adding 20 scans with resolution of 2 cm⁻¹.

3. Results and discussion

Fig. 1 compares the conversion of CH₄ over Pd catalyst supported on ZrO₂ (Pd/ZO) and on hydrophilic silica A130 (Pd/A130). The value $t = 0$ is assigned when the reactor reaches a temperature of 325 °C. The conversion of the Pd/ZrO₂ catalyst is almost constant, around 18%, during 40 h of reaction, which is in agreement with what has been reported in the literature [30]. On the other hand, the Pd/SiO₂ catalyst

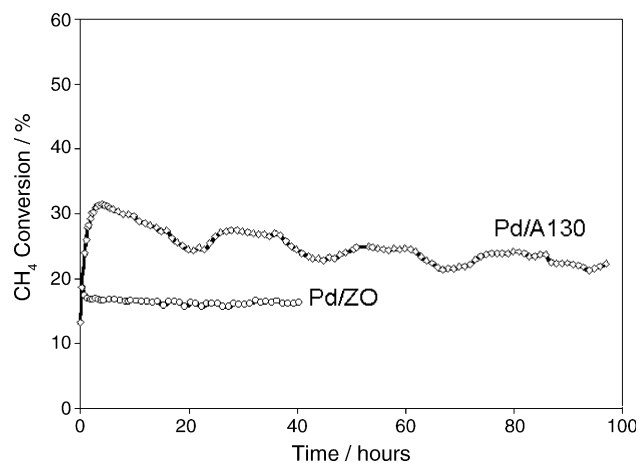


Fig. 1. Methane conversion over time of the Pd/ZO and Pd/A130 catalysts. Reaction conditions: 1.5% CH₄; 6% O₂; total flow = 90 cm³ min⁻¹, balanced in He; temperature = 325 °C; catalyst mass = 0.2 g.

shows increasing conversion during the first 3 h, reaching 32% conversion, and then decreases slowly to a conversion of about 22% after 96 h of reaction. During the deactivation the silica supported catalyst shows an oscillatory behavior not observed in the Pd/ZrO₂ catalyst. This pattern is reproducible and must be related with changes in the catalytic surface, but it requires more detailed studies to give an explanation of this phenomenon. It is important to note that the initial activation of catalyst Pd/A130 cannot be attributed to the elimination of Cl, since neither the support nor the precursor contained that species.

To study the activation of the Pd/A130 catalyst in more detail, a fresh sample of catalyst was subjected to consecutive cycles of oxidation pretreatment followed by reaction. The experimental procedure is similar to that described above. After the catalyst reached its maximum activity at 325 °C, the flow of methane was stopped and the catalyst was kept under pure O₂ for 30 min. Then methane was added again to the gas feed and the effluent was analyzed to determine the conversion of methane in time. The results of this experiment are shown in Fig. 2. It is seen that immediately after the first treatment in pure O₂ the methane conversion decreases, but as the reaction continues the catalyst recovers a conversion similar to that observed before the O₂ treatment (Fig. 2, zone 2). A second treatment in pure O₂ at 500 °C for 30 min decreases slightly more the methane conversion, but again under the reaction mixture the conversion increases to the value found initially before the treatments in O₂ (Fig. 2, zone 3). These results clearly show that a treatment in oxygen reduces the catalytic activity, and that activation occurs in the presence of the reacting mixture, apparently by changes in the surface of the catalyst, as has been proposed in the literature for Pd/Al₂O₃ catalysts [13,18,32].

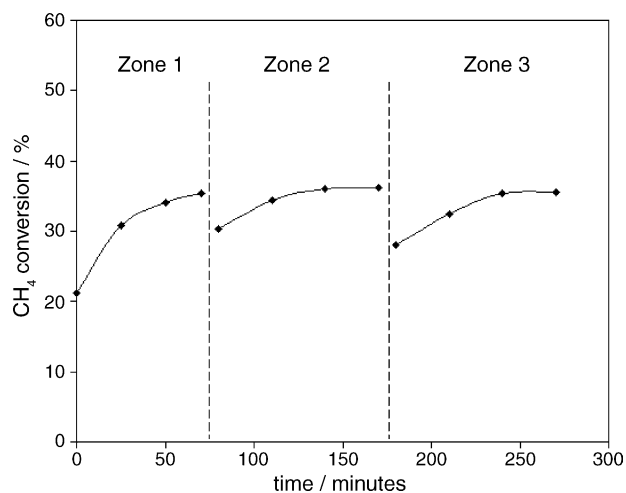


Fig. 2. Effect of treatment with O₂ at 325 and 500 °C on the activity of the Pd/A130 catalyst. Zone 1: activation of the catalyst under the same conditions as those of Fig. 1; Zone 2: treated with O₂ at 325 °C for 30 min (first effluent sample 5 min after restarting the flow of CH₄); Zone 3: treated with O₂ at 500 °C for 30 min (first effluent sample 5 min after restarting the flow of CH₄).

On the other hand, the slow deactivation of the Pd/A130 catalyst shown in Fig. 1 does not agree with the results presented by Muto et al. [25]. They reported a steady decrease in the methane conversion, from 25 to 12%, during a 7 h period at 450 °C over a 0.5% Pd/SiO₂ catalyst. According to these authors, the decrease in activity is related to the decrease in dispersion from 10% in the fresh catalyst to 5.6% after the reaction. The Pd/A130 catalyst used for 96 h has a dispersion of 28.2%, which is almost the same as that found for the fresh (unused) catalyst as seen in Table 1. Thus, the deactivation process cannot be explained by a decrease in the number of active sites. The deactivation of the Pd/A130 catalyst might be explained by a slow formation of Pd hydroxide as suggested by Roth et al. [33]. These authors suggested that the presence of Pd(OH)₂ would cause the slow deactivation of the 5% Pd/Al₂O₃ catalyst at a reaction temperature of 350 °C.

It should be pointed out that the maximum conversion found for the catalyst supported on silica, Pd/A130, is almost twice that of the catalyst supported on zirconium oxide, Pd/ZO, at a reaction temperature of 325 °C. Even after 96 h of reaction, the Pd/A130 catalyst is still more active than the Pd/ZO catalyst. As shown below, the greater activity of the Pd/A130 catalyst can be explained by the lower inhibiting effect of water in the catalysts supported on silica as compared to the catalysts supported on zirconium oxide.

3.1. Inhibiting effect of H₂O

Considering a reaction order of -1 with respect to the water concentration, and neglecting inhibition by CO₂, Yeung et al. [42] suggested that the rate of methane combustion in excess O₂ at low temperatures (below 500 °C) over Pd/ZrO₂ catalysts may be represented by the empirical formula:

$$r = k_{\text{app}} \frac{[\text{CH}_4]}{[\text{H}_2\text{O}]} \quad (1)$$

Assuming a plug-flow reactor, they derived the expression to calculate the apparent reaction constant (k_{app}):

$$k_{\text{app}} = \frac{2F_{\text{CH}_4}}{n_{\text{Pd}}} \left(\ln \left(\frac{1}{1-x} \right) - x \right) \quad (2)$$

where n_{Pd} represents the number of Pd sites on the surface, x the conversion of methane, and F_{CH_4} the methane flow at the reactor inlet. By using Eq. (2) k_{app} can be calculated when no water is added to the feed (dry feed) and the water present in the reactor is only generated by the methane combustion.

Different experimental procedures can be used to determine the reaction order with respect to water. One of them is to determine the reaction rate by changing the partial pressure of water fed to the reactor, keeping the other variables (temperature, CH₄ and O₂ concentration, and total flow) constant. In this work, and with the objective of studying the influence of the water produced during the reaction, an alternative procedure was used. In this case, the

mass of catalyst loaded in the reactor was varied and the value of k_{app} was determined for each case. With a lower amount of catalyst the methane conversion decreases, lowering also the water concentration within the reactor. Thus, in the absence of diffusional effects due to mass and heat transfer, a constant value of k_{app} at a given temperature for different mass of catalyst loaded would indicate that the order with respect to water assumed in Eq. (1) is correct. As it will be shown below, using this procedure it is possible to study the reaction order with respect to water and the effect of diluting the catalyst without adding water to the reactor feed, thus keeping a very low water partial pressure.

First, the experimental procedure just described was used to verify the order of -1 with respect to the concentration of water in the gas phase reported in the literature for Pd catalysts supported on zirconium oxide. Different amounts of Pd/ZO catalyst were diluted using pure ZO support to keep a constant loading of 0.2 g (catalyst + support) in the reactor. Table 2 shows the catalyst and support loadings used in each experiment, as well as the conversions obtained at 325 °C in each case. Since the previous results (Fig. 1) indicated that the Pd/ZO catalyst shows a constant conversion over time, the conversion reported in Table 2 corresponds to the stable conversion of the catalysts. With the conversion values at 325 °C and using Eq. (2) the apparent rate constant, k_{app} , was calculated. These values are also reported in Table 2.

As expected, the results in Table 2 show that methane conversion decreases as the amount of catalyst Pd/ZO decreases. The decrease in the conversion also reduces the concentration of water generated by the reaction, but the calculated rate constant k_{app} is essentially the same in all cases. Indirectly, this confirms that Eq. (2) considers correctly the order -1 for the dependence of the methane conversion on water concentration in the gas phase. Conversion values obtained at different temperatures between 50 and 325 °C were used to calculate k_{app} at the various temperatures. Using these values, shown in the Arrhenius plot in Fig. 3 for the pure catalyst and the most diluted one, the apparent activation energy of the reaction (E_a) was calculated for each sample. These values are

Table 2

Methane conversion (x), and apparent reaction constant (k_{app}) for catalyst Pd/ZO and Pd/ZO + support (ZO) mixtures at 325 °C, keeping the total mass at 0.2 g

Sample	x (%)	k_{app} (mol CH ₄ /mol Pd s)	E_a [kcal mol ⁻¹]
0.20 g Pd/ZO	18.2	0.0039	41
0.10 g Pd/ZO + 0.10 g ZO	12.1 (12.7)	0.0033	40
0.06 g Pd/ZO + 0.14 g ZO	9.1 (8.9)	0.0031	41
0.02 g Pd/ZO + 0.18 g ZO	5.7 (5.8)	0.0035	42

Values in parenthesis correspond to methane conversion of undiluted catalyst.

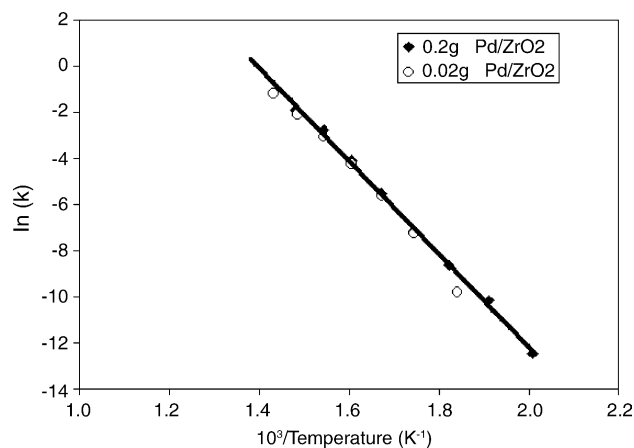


Fig. 3. Arrhenius plot for different loadings of Pd/ZrO₂ catalyst (◆): 0.2 g Pd/ZrO₂; (○): 0.02 g Pd/ZrO₂ diluted with 0.18 g ZrO₂.

reported in Table 2. The activation energies for different catalyst loadings show only small differences that can be considered within experimental error. The average value of E_a (41 kcal mol⁻¹) agrees quite well with the value of 42 kcal mol⁻¹ reported by Yeung et al. [42] for a 7% Pd/ZrO₂ catalyst that, similarly to this work, was oxidized in situ before determining the activity.

Dilution of the catalyst using an inert species, usually the support, is a common procedure when a given bed volume is to be adjusted. However, considering that in the case of the combustion of methane over supported Pd catalysts it has been suggested that the possible adsorption of water may affect the catalysts' activity [44], it was considered important to verify whether dilution of the catalyst by the support would affect the activity measurements. With that purpose, the previous experiments were repeated, loading the same amounts of 1% Pd/ZrO₂ catalyst reported in Table 2, but without adding any support (undiluted samples). The results obtained for methane conversion against reaction time, shown in parenthesis in the same table, were almost identical to those obtained with the diluted catalysts, showing that indeed the support does not affect the catalyst's activity.

To determine the reaction order with respect to water for the Pd/SiO₂ catalyst, the same procedure described for the Pd/ZrO₂ catalyst was used, mixing different amounts of catalyst with the A130 support to keep a total catalyst + support loading of 0.2 g. With this catalyst, however, preliminary studies of the effect of catalyst dilution showed an unexpected behavior, so the catalyst activation procedure had to be modified.

In Fig. 4, curve (A) shows methane conversion against reaction time when 0.02 g of 1% Pd/A130 catalyst were mixed with 0.18 g of A130 support and calcined in the reactor as usual. Curve (B) shows the results when only 0.02 g of 1% Pd/A130 catalyst were loaded without adding support. It is seen that the conversion for the catalyst mixed with the support is lower than that of the pure catalyst. It seems that the presence of the support affects the catalyst's

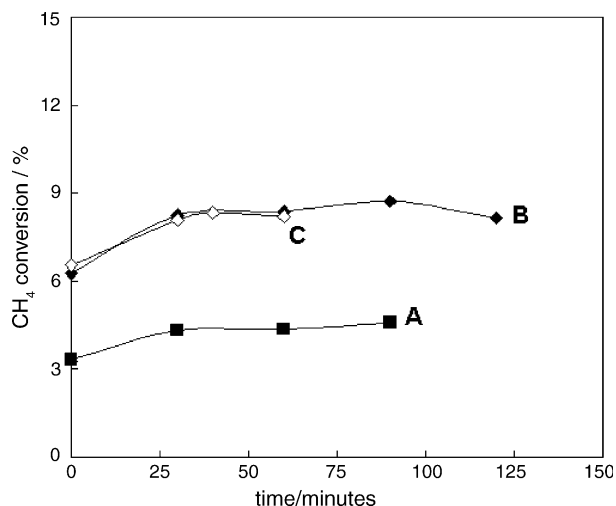


Fig. 4. Methane conversion over time of catalyst Pd/A130 using different calcination procedure for the catalysts and support. (A): Calcining the physical mixture of 0.02 g Pd/A130 diluted with 0.18 g A130; (B): calcining 0.02 g Pd/A130 undiluted; (C): calcining previously 0.02 g Pd/A130 and then mixing physically with the support. Same reaction conditions as in Fig. 1.

activity probably through a phenomenon like the one proposed by Burch [44], related to the support's capacity to adsorb water. However, if the pure catalyst is calcined at 500 °C and is then mixed with the support, the conversion against reaction time, showed in curve (C), is almost the same as if it had been loaded alone into the reactor. It is clear therefore, that dilution with the support does not have an effect during the reaction, but rather during the calcination and activation pretreatments. Probably the dilution of the catalyst with silica produces a more humid environment in the bed during calcination, affecting the catalyst's final activity, as it has been previously reported [20]. Considering these observations, in the experiments that involved mixtures of Pd/A130 catalyst with the support, the catalyst was calcined before mixing it with the inert silica.

The different amounts of 1% Pd/A130 catalyst and A130 support used, and the results of conversion against reaction time at a temperature of 325 °C are shown in Fig. 5(A). Assuming a priori an order of -1 for water, the conversion data from Fig. 5(A) and Eq. (2) were used to estimate the value of the apparent constant, k_{app} , for the reaction. The values of k_{app} versus time for the different samples are showed in Fig. 5(B). It is seen that there is a clear tendency to decreasing values of k_{app} as the mass of Pd/A130 catalyst in the reactor decreases, indicating that Eq. (1) does not adequately represent the reaction order of water in the Pd catalysts supported on silica, under the conditions used in these experiments.

To find the order with respect to water that best represents the data of the conversion of Pd shown in Fig. 5(A), we can write Eq. (1) for any order α as:

$$r = k_{app} [\text{CH}_4] [\text{H}_2\text{O}]^\alpha \quad (3)$$

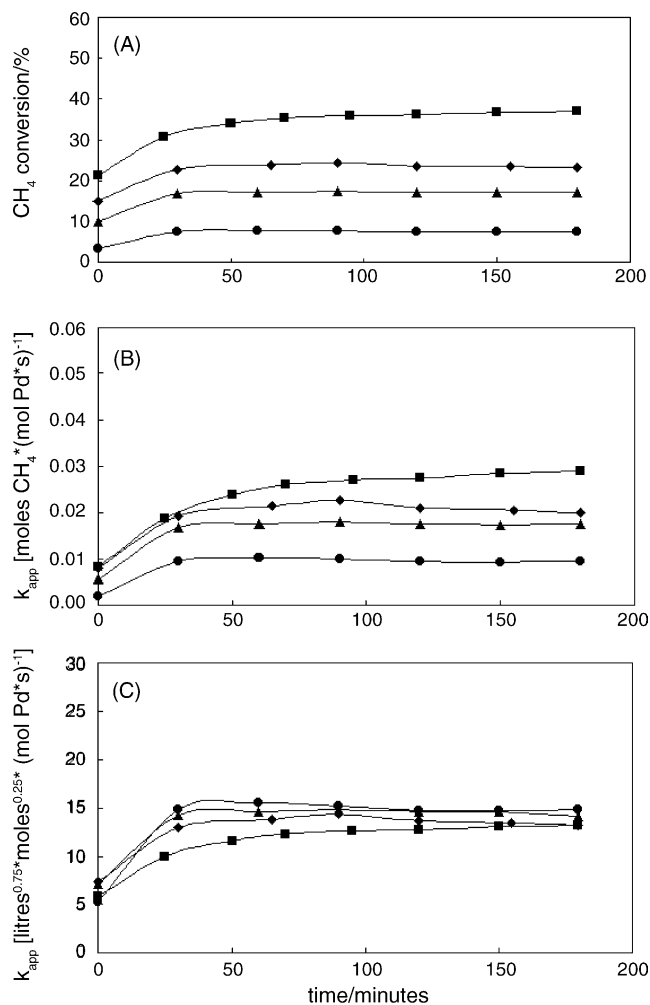


Fig. 5. (A) Methane conversion over time using different loadings of Pd/A130 catalyst diluted with the A130 support. (B) k_{app} calculated assuming an order of -1 with respect to water (Eq. (2)). (C) k_{app} calculated assuming a reaction order of -0.25 with respect to water (Eq. (4)). Same reaction conditions as in Fig. 1. Nomenclature: (■) 0.2 g Pd/A130; (◆) 0.1 g Pd/A130 + 0.1 g A130; (▲) 0.06 g Pd/A130 + 0.14 g A130; and (●) 0.02 g Pd/A130 + 0.18 g A130.

and the integrated equation to calculate k_{app} assuming a plug-flow reactor in the form:

$$k_{app} = \frac{F_{CH_4}}{n_{Pd}[CH_4]_0(2[CH_4]_0)^\alpha} \int_0^x \frac{dx}{(1-x)(x)^\alpha} \quad (4)$$

where the symbols have the same meaning as in Eq. (2), and $[CH_4]_0$ is the concentration of methane at the reactor inlet.

Eq. (4) can be solved by numerical integration to get k_{app} at different values of α . The optimum value of α , which minimizes the deviation in the values of k_{app} calculated for the Pd/A130 catalyst and its mixtures with the A130 support, can then be easily found. For the data given in Fig. 5(A) it was found that the value of α that yields the smallest deviation in the values of k_{app} is -0.25 . Fig. 5(C) shows the values of k_{app} versus time calculated using Eq. (4) and an order $\alpha = -0.25$. There is good agreement of the k_{app} values

in the region where the conversion is relatively constant over time for the different samples. This result is somewhat surprising, since in principle a change would not have been expected in the order with respect to water in Pd catalysts supported on silica, in relation to the -1 order found in Pd supported on alumina or zirconium oxide for this reaction temperature.

To explain the lower apparent water reaction order found for Pd/SiO₂, the simple model proposed by Ciuparu and Pfefferle [35] and Kikuchi et al. [36], can be used. These authors assumed that the rate-controlling step is the CH₄ adsorption on Pd particles, and that the coverage by species other than water is negligible. Therefore, considering that water adsorption can be modeled by the Langmuir isotherm, they proposed that the rate of CO₂ production can be expressed by the equation:

$$r = \frac{k_r [CH_4]}{1 + K_{H_2O} [H_2O]} \quad (5)$$

which in terms of the concentration of methane, $[CH_4]_0$, and water, $[H_2O]_0$, at the reactor inlet leads to the expression:

$$r = \frac{k_r [CH_4]_0 (1-x)}{1 + K_{H_2O} ([H_2O]_0 + 2x[CH_4]_0)} \quad (6)$$

where K_{H_2O} is the equilibrium constant for water adsorption on the surface of Pd particles. Eqs. (5) and (6) show clearly that the apparent water reaction order depends on the value of K_{H_2O} and the water concentration. If $K_{H_2O}[H_2O] \gg 1$, Eq. (5) becomes Eq. (1), and the apparent order for water is -1 , as in the case of the Pd/ZrO₂ catalyst. Lower K_{H_2O} values can lead to any apparent reaction order for water from 0 to -1 .

Using Eq. (6), Kikuchi et al. calculated the water adsorption enthalpy (ΔH_{ads}) on the surface of Pd particles supported on different solids (Al₂O₃, SnO₂ and SnO₂-NiO), adding different concentrations of water at the reactor inlet. They found that the support can considerably affect the value of ΔH_{ads} . When Pd is supported on Al₂O₃, the highest value for ΔH_{ads} was found ($-11.7 \text{ kcal mol}^{-1}$), while the lowest value ($-7.1 \text{ kcal mol}^{-1}$) is reported for Pd supported on Al₂O₃-NiO. Because of the exponential dependence of the water adsorption constant on the value of ΔH_{ads} , important changes can be expected in the value of K_{H_2O} for different supports, and therefore in the reaction order with respect to that species.

To estimate the value of K_{H_2O} and k_r for our Pd/SiO₂ catalysts under dry conditions, i.e. without adding water to the feed, a similar procedure to that previously described to obtain the apparent order α was used. Starting from the plug-flow reactor design equation, and using the rate expression given by Eq. (6), the expression for the reaction constant k_r is as follows:

$$k_r = \frac{F_{CH_4}}{n_{Pd}[CH_4]_0} \int_0^x \frac{(1 + K_{H_2O}([H_2O]_0 + 2x[CH_4]_0)) dx}{(1-x)} \quad (7)$$

Using Eq. (7), the value of $K_{\text{H}_2\text{O}}$ that gave the best fit with our experimental data was estimated, i.e. the value of $K_{\text{H}_2\text{O}}$ leading to the smallest change in the value of the reaction constant k_r calculated with Eq. (7) for the different catalyst loadings is determined.

The value of the water adsorption constant that gave the smallest change in the value of k_r calculated from the conversion data of catalyst Pd/A130 (Fig. 5A) was 9500 l mol^{-1} . For this value of $K_{\text{H}_2\text{O}}$, Eq. (7) leads to an average value of k_r equal to 490 s^{-1} .

3.2. Effect of the hydrophobicity of the support

To analyze if the hydrophobicity of silica has some effect on the reaction order with respect to water, the activity of Pd catalysts supported on hydrophobic silica R972 and for mixtures of variable amounts of the catalyst with silica R972 was studied. Because of the hydrophobic character of silica R972, an organic salt (palladium acetyl acetonate, $\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$) was dissolved in acetone to be used as precursor. The hydrophobicity of silica R972 is due to replacement of the superficial OH groups by methyl groups, which can easily be studied by IR spectroscopy. The methyl groups have an absorption band at 2900 cm^{-1} , while isolated OH groups are characterized by a band at 3745 cm^{-1} . Fig. 6 shows the IR spectra of Aerosil R972 silica, the Pd/R972 catalyst previously calcined at 400°C for 1 h, and the Pd/

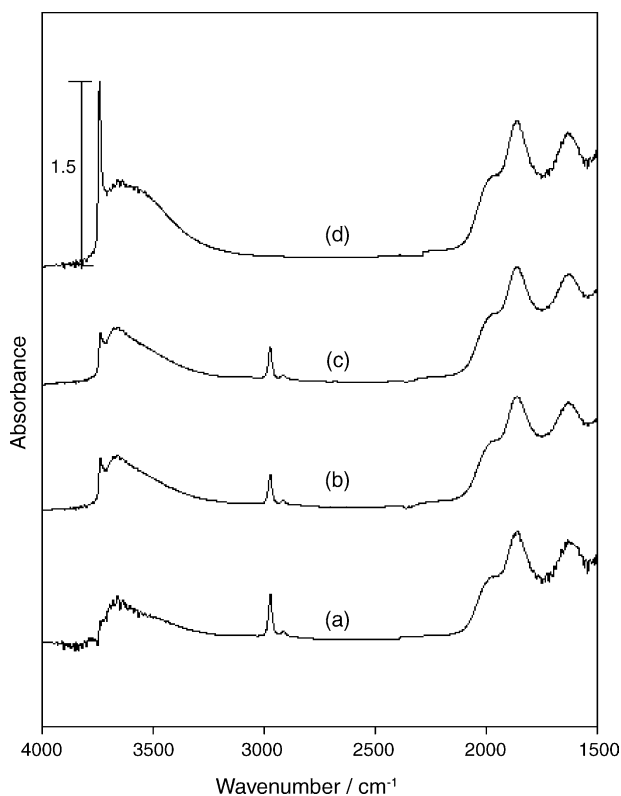


Fig. 6. IR spectra. (a): R972 support; (b): catalyst Pd/R972 calcined for 1 h at 400°C , unused; (c): catalyst Pd/R972 used in experiment to determine reaction order; (d): A130 support.

R972 catalyst after being used in the experiment. Fig. 6 also includes the IR spectrum of Aerosil 130 for comparison. It is seen that the IR spectrum of the pure silica R972 support, spectrum (a), shows only the methyl group peak at 2900 cm^{-1} . Spectrum (b), corresponding to the catalyst Pd/R972 previously calcined at 400°C , is similar to that of the pure support, showing the methyl group peak at 2900 cm^{-1} and a small band corresponding to isolated OH groups at 3745 cm^{-1} . As seen in spectrum (c), the use of the catalyst in the experiment at 325°C in the presence of the reacting mixture does not cause important changes with respect to calcined and unused catalyst Pd/R972. The spectrum of the used catalyst still shows the methyl group band and a weak band corresponding to a low concentration of OH groups. Therefore, the hydrophobicity of the support was retained during the experiments. It should be mentioned that calcination temperature of the catalyst is limited to 400°C for 1 h, since at higher temperatures the methyl groups disappear completely being replaced by OH groups, thus the silica R972 would lose its hydrophobic character. The spectrum of catalyst Pd/R972 calcined at 425°C for 1 h (not included) indicates the absence of the methyl groups and their replacement by OH groups, with a spectrum very similar to (d), which corresponds to the hydrophilic silica Aerosil 130. In the absence of Pd, silica R972 can be calcined at a higher temperature (500°C , 2 h) without detectable loss of the methyl groups.

Fig. 7(A) shows the conversion versus reaction time curves for the catalyst Pd/R972 and its mixtures with this support. It is seen that the shapes of the curves and the conversion value reached are very similar to those obtained in the case of catalyst Pd/A130. Again there is an activation of the catalyst followed by a period in which conversion is almost constant. As seen in Fig. 7(B), and similarly to what was found in the case of Pd supported on Aerosil 130, calculation of the apparent constant, assuming an order of -1 with respect to the concentration of water, yields a k_{app} value that decreases as the mass of catalyst Pd/R972 decreases, indicating that the assumed order is incorrect. The use of Eq. (4) to get the optimum value of the order α leads to the same reaction order, $\alpha = -0.25$, found for the Pd catalyst supported on hydrophilic silica Aerosil 130, as can be seen in Fig. 7(C). Using Eq. (7), and following the same procedure described for the 1% Pd/A130 catalyst, values of $k_r = 473 \text{ s}^{-1}$ and $K_{\text{H}_2\text{O}} = 9000 \text{ l mol}^{-1}$ are obtained, almost identical to the values calculated for the catalyst supported on the hydrophilic silica Aerosil 130. It is clear, then, that the hydrophobicity of the support does not affect the reaction order with respect to water in the catalysts supported on silica, when no water is added to the feed.

3.3. Effect of the addition of water to the feed stream

The effect of adding 3% of water to the feed on the activity of the Pd/A130 catalyst is shown in Fig. 8(A). Curve (1) shows conversion against time for the Pd/A130 catalyst

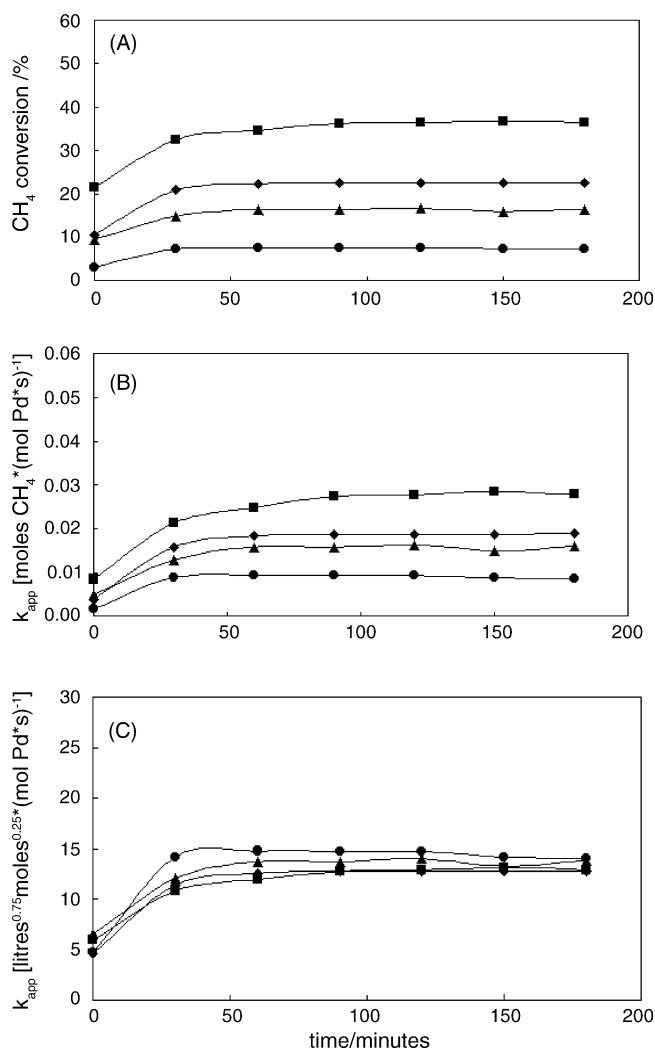


Fig. 7. (A) Methane conversion over time using different loadings of Pd/R972 catalyst diluted with the R972 support. (B) k_{app} calculated assuming an order of -1 with respect to water (Eq. (2)). (C) k_{app} calculated assuming a reaction order of -0.25 with respect to water (Eq. (4)). Same reaction conditions as in Fig. 1. Nomenclature: (■) 0.2 g Pd/R972; (◆) 0.1 g Pd/R972 + 0.1 g R972; (▲) 0.06 g Pd/R972 + 0.14 g R972; and (●) 0.02 g Pd/R972 + 0.18 g R972.

without adding water to the feed. It is seen that the catalyst reaches a maximum conversion value after an activation period of 2–3 h and then decreases slowly with time on stream. When 3% water is added to the feed, curve (2), the conversion drops mainly due to the inhibiting effect of water, and continues to decrease slightly as water is kept in the feed. Once the water flow is stopped, after 2 h of reaction, the catalyst returns to conversion value lower than those obtained before the addition of water (approximately 76% of the conversion value before adding water to the feed). After comparing curves (1) and (2), it is clear that the presence of water accelerates the deactivation of the Pd/A130 catalyst. This result is in agreement with the finding of Nomura et al. [29] for Pd catalysts supported on alumina. These authors attribute the deactivation of the Pd/Al₂O₃ catalyst, which differs with the stability of the Pd/ZrO₂ catalyst, to the

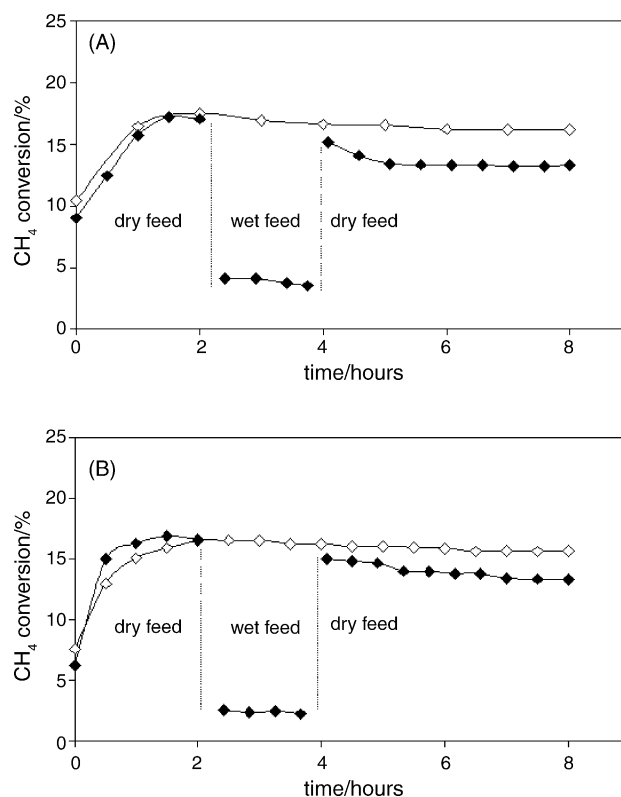


Fig. 8. Effect of water addition to the reactor feed. (A) Pd/A130 catalyst; curve (1): dry feed, curve (2): 3% of water. (B) Pd/R972 catalyst; curve (1): dry feed, curve (2): 3% of water. Same reaction conditions as in Fig. 1.

greater affinity of alumina for water. Using Eq. (7) to calculate the value of K_{H_2O} for the Pd/A130 catalyst, and considering the 3% water concentration added to the feed, a value of $K_{H_2O} = 8500 \text{ l mol}^{-1}$ is obtained. This result is very similar to the value calculated in the experiments without the addition of water.

In the case of the catalyst prepared with hydrophobic silica, Pd/R972, the effect of the addition of water in the feed is similar to that seen with catalyst Pd/A130, as can be observed in Fig. 8(B). Again, water accelerates the catalyst's deactivation in a proportion that relatively similar to that seen with Pd/A130, leading to 79% of the activity it had before the addition of water to the feed. Therefore, the hydrophobicity of the support does not seem to play an important role in the catalyst's deactivation, within the time range considered in the experiment (8 h). Unfortunately, the comparison between both catalysts could not be made at longer reaction times because of the progressive decrease in the concentration of surface methyl groups in silica R972 with time on stream. During IR experiments (not shown) of the catalyst Pd/R972 at different reaction times, a considerable decrease in the amount of methyl groups was observed after 12 h or more.

The inhibiting effect of water, however, was more pronounced for the catalyst Pd/R972 than for the catalyst Pd/A130. In fact, the value of the equilibrium constant (K_{H_2O}) calculated from Eq. (7) for the catalyst Pd/R972 is equal to

23,700 l mol⁻¹, which is substantially larger than in the case of Pd/A130. This greater effect for the Pd/R972 catalyst could be explained using the ideas proposed by Burch [44]. According to this author, a high water affinity of the support can decrease the local water partial pressure in the surrounding of a PdO particle. Therefore, this is probably the case for the Pd/A130 catalyst, in which the PdO is supported on a hydrophilic material that initially captures an important amount of water. On the other hand, in the Pd/R972 catalyst, the support cannot adsorb water, and the local water concentration is higher, thus explaining the higher water inhibition effect observed for this catalyst. When no water is added to the feed and only the small amount of water produced by reaction is present in the gas phase, the support's hydrophobicity play a less important role on the water inhibition phenomena and both catalysts seems to be inhibited by water in a similar degree.

4. Conclusions

The water generated during the complete oxidation of methane on silica supported Pd catalysts has a smaller inhibiting effect compared to the activity of Pd catalysts supported on alumina or zirconium oxide. The results of this work show that, under identical experimental conditions, the apparent reaction order with respect to water is -0.25 for the Pd/SiO₂ catalyst and, in agreement with the literature, order -1 for the Pd/ZrO₂ catalyst.

Furthermore, when no water is added to the feed, it was shown that the degree of hydrophobicity of the silica does not affect significantly the catalytic behavior. Both apparent reaction order with respect to water and the activation and deactivation processes are comparable for the two silica supported Pd catalysts. When water is added into the feed, however, the different hydrophobicity of the supports affects the inhibition caused by the adsorption of water on the surface of the catalysts. The addition of water also accelerates the deactivation process of the silica supported Pd catalysts.

Acknowledgements

The financial support by Conicyt (Project Fondecyt 8000015 and Fondap 1198000-2) is gratefully acknowledged.

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