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Methane Combustion on Pd/SiO_2 Sol Gel Catalysts

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Surface properties and catalytic activity changes of Pd/SiO_2 catalysts prepared by sol-gel processing have been investigated by evaluating the specific surface area, porosity, metal dispersion, surface acidity, and surface composition. As a comparison, Pd/SiO_2 catalysts prepared by impregnation of SiO_2 obtained by the sol-gel method were also studied. Both series of catalysts were tested in cycles of methane combustion. It has been found that the pH of gelation modifies strongly the porosity and surface area of the catalysts. However, no significant changes were observed in the metal dispersion. XPS results showed that for the catalysts obtained by the sol-gel procedure the Pd/Si surface atomic ratio does not change before or after the combustion cycle. However, in those catalysts prepared by the impregnation method, a significant decrease in the Pd/Si ratio was observed. The catalytic activity in the methane combustion under stoichiometric mixture of diluted CH_4/O_2 was studied at different temperatures from 473 K up to the temperature required for a total conversion of all the catalysts. It was found that the activity is higher after their use in the catalytic reaction. This behaviour is attributed to the presence of $Pd_{\delta+}$ species which improve the catalytic activity.

INTRODUCTION

The catalytic combustion of hydrocarbons is becoming of increasing importance to control the emissions of the volatile organic compounds (VOC). It may reduce drastically the temperature required for a complete combustion compared with the thermal process (1–3). Thus, while thermal combustion proceeds at temperatures higher than 1300 K, in the catalytic process the temperature for a complete decomposition of the organic compounds is lower than 1000 K. Additionally, an important decrease in the NO_x emission by more than 90% is produced (4).

Catalysts able to perform combustion are normally divided in two groups: noble metals for which reaction may start at temperature as low as room temperature and transition metal oxides which are less efficient but which are also more resistant towards high temperature operation. Most of the studies have been focused on noble metal-supported catalysts, and among them, catalysts based on platinum and palladium have received special attention (5–8). It has been found that under oxidising conditions, Pt is better than Pd for the combustion of higher alkanes and olefins (9, 10). However, methane combustion is easier over Pd in an oxygen-rich atmosphere, whereas Pt catalysts are more active when the reactant mixture is methane rich (11). The nature of the support has also been investigated. Thus, TiO_2, SiO_2, and Al_2O_3 have been widely studied. The addition of La_2O_3, CeO_2, and ZrO_2 to enhance the stability and catalytic activity has also been assayed (12). The decrease in the activity of metal-supported catalysts in the mentioned reaction, by sintering induced by performance at high temperature and by the presence of water in the gas stream, represents one of the main problems. Dalla Betta *et al.* (13), have studied the oxidation of methane on Pd-supported catalysts using different metal precursors ($PdCl_2$ or $Pd(NH_3)_2(NO_2)$) and supports (Al_2O_3 or ZrO_2). They report that the reaction is structure insensitive. Similar conclusions were reached by Cullis and Willat (14). On the contrary, Baldwin and Burch (15) found a change in TOF of two orders of catalysts with no correlation between particle size and TOF, while Hicks *et al.* (16, 17) reported that the TOF is higher for larger Pd particles. On the other hand, Sekizawa *et al.* (18) found that in the combustion of methane on mixed oxide-supported palladium catalysts, Pd particle size is an important factor in determining catalytic activity. Sol-gel processing may provide an appropriate way to prepare supported metal catalysts in which the sintering of metal particles is strongly restricted (19, 20). A greater degree of control over the catalyst preparation can be achieved in comparison to the traditional method of preparation. Advantages include among others: higher surface area, well defined pore size distribution, higher homogeneity, and improved thermal stability of the supported metals (21). Sol-gel Pd/SiO_2 catalysts have been reported by López *et al.* (19–21). Different parameters, such as the pH of gelation, or metal precursor, may strongly affect the surface properties of the catalysts. Preparation under acid conditions leads to essentially microporous solids, whereas under basic conditions an important proportion of mesopores are present. This fact is

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important to modify the selectivity during a hydrogenation test reaction.

In the present work the catalytic combustion of methane has been studied over Pd/SiO_2 sol-gel catalysts. The effect of the pH of gelation and the way of incorporating the palladium on the surface properties and catalytic behaviour are investigated. The solids were characterised by nitrogen adsorption at 77 K, H_2 chemisorption measurements, TEM studies for particle size evaluation, and XPS experiments to determine the chemical state of the Pd and the surface composition. The combustion of CH_4 with a stoichiometric amount of oxygen was used as the test reaction.

EXPERIMENTAL

A mixture of 30 ml of tetraethyl orthosilicate (TEOS) with 20 ml of ethanol and 0.1145 g of $Pd(acac)_2$ dissolved in acetone was stirred and refluxed at 318 K. Then, 19 ml of aqueous solutions at different pH (3-HCl, 3-H_2SO_4, 5-CH_3COOH, and 9-NH_4OH) were added to the mixture. The reflux was maintained until the formation of the gels were achieved. Then, the temperature was increased to 353 K and kept constant for 1 h. The obtained wet gel was dried at 383 K for 6 h and then calcined in air at 723 K for 4 h. Hereafter the series of catalysts prepared by this procedure will be referred as Pd/SiO_2 (SG). Using a similar procedure, but without the addition of $Pd(acac)_2$ a series of supports was obtained. These solids, after calcination in air at 723 K for 4 h, were impregnated with a toluene solution of $Pd(acac)_2$, dried overnight at 393K and calcined in air at 723 K. In all samples, the Pd loading was 0.5 wt%. Prior to their characterisation or catalytic use the solids were reduced *in situ* in flowing H_2 at 773 K.

To evaluate the specific surface area, pore volume, and average pore diameter, nitrogen adsorption isotherms at 77 K in the relative pressure range 0.05 to 0.995 were carried out in a Micromeritics Model Gemini 2370 apparatus. Hydrogen chemisorption at 343 K was carried out in a volumetric system to evaluate the H_2 uptake and H/Pd ratio.

TEM was used to observe the supported palladium particles. These experiments were performed in a Jeol Model JEM-1200 EX-II System. The samples were prepared by the extractive replica procedure.

XPS studies were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant-pass energy mode and unmonochromatized Mg Kα X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA and 12 kV. The surface Pd/Si ratios were estimated from the integrated intensities of Pd 3d and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors (25). The line of Si 2p at 103.4 eV was used as an internal standard.

Catalytic combustion of methane over supported palladium catalysts was evaluated in a conventional flow reactor at atmospheric pressure. In each experiment 200 mg of catalysts were used. The calcined sample was heated in He up to 473 K and then the carrier gas was switched to 50 cc/min of the reactant mixture containing CH_4 (1 vol%), O_2 (2 vol%) and He (balance). The activity was measured at different temperatures from 473 K up to total conversion, using a heating rate of 1°/min. Afterwards, the sample was cooled down to 473 K and it was reduced *in situ* in flowing hydrogen (50 cc/min) up to 773 K for 1 h. Then the sample was cooled down to 473 K and the reducing gas was switched to He as the carrier. After 30 min of stabilization at this temperature, the carrier gas was switched to the reactant gaseous mixture and a new cycle of combustion was performed. Finally, once total CH_4 conversion was achieved the sample was cooled down in He to 473 K, switched to the reactant mixture, and a new cycle was carried out. The effluents of the reactor were analysed by an on-line gas chromatograph and in some experiments, a Quadupole Mass Spectrometer, Hiden HPT 20, was used to detect small traces of products.

RESULTS AND DISCUSSION

Figure 1a displays the nitrogen adsorption isotherms for one of the series of the prepared Pd/SiO_2 catalysts. Significant differences in the adsorbed amount, as well as in the shape of the isotherms, can be noted. Thus, the catalysts prepared by gelation at pH 3 in the presence of H_2SO_4, or HCl give a type-I isotherm in the BDDT classifications, indicating essentially the presence of a microporous structure. A significant change, both in the adsorbed amount and in the shape of the isotherm, is observed in the sample prepared at pH 5. The obtained isotherm suggests the presence of micro- and mesopores and the amount of nitrogen uptake is the highest of the prepared Pd/SiO_2 (SG) catalysts. Moreover, as is well known, the shape of the isotherm in the low pressure range may provide a qualitative idea on the pore size distribution. Thus, for a given adsorbate, a sharp knee of the isotherm indicates a high adsorption in the low pressure range and consequently a pore size distribution consisting mainly of fine pores, as it clearly appears in Fig. 1a for samples prepared in an acid medium. Considering the microporous structure of the solids, it is clear that it is not possible to use a type-I isotherm for BET analysis to evaluate a specific surface area; therefore a Dubinin–Raduskevitch–Kaganer (DRK) analysis should be carried out. Figure 1b shows the linear DRK plots for the same series of Pd/SiO_2 catalysts. It can be noted that the plots of log X against $(\log(P^\circ/P))^2$ exhibit a long straight portion for all the samples. In the case of the samples obtained by gelation at pH 5 and 9 a deviation from the linearity at high pressure can be seen. This may be associated with the presence of meso- and macropores in these solids. The higher proportion of micropores in the solids obtained at pH 3–5 is explained by taking into account that at these pH values the rate of hydrolysis

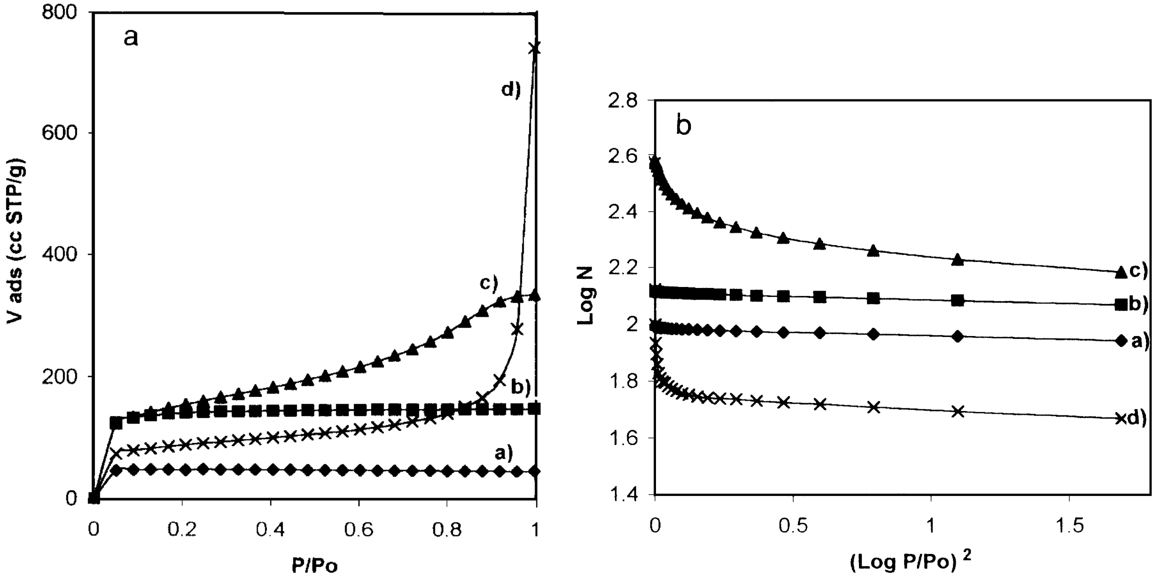

FIG. 1. (**a**) Nitrogen adsorption isotherms at 77 K for Pd-SiO$_2$ (SG) catalysts: (a) pH 3-HCl (A); (b) pH 3-H$_2$SO$_4$ (B); (c) pH 5-CH$_3$COOH (C); (d) pH 9-NH$_4$OH (D). (**b**) DRK plots of the nitrogen adsorption isotherms at 77 K for Pd-SiO$_2$ (SG) catalysts: (a) pH 3-HCl (A); (b) pH 3-H$_2$SO$_4$ (B); (c) pH 5-CH$_3$COOH (C); and (d) pH 9-NH$_4$OH (D).

is higher, producing a highly branched polymeric product. Similar results were obtained for the series of catalysts prepared by impregnation of the SiO$_2$ obtained by the sol-gel procedure. Table 1 summarizes the specific surface area, estimated by the nitrogen adsorbed amount from BET and DRK equations, pore volume, and average pore diameter obtained from the nitrogen uptake at saturation, according to Gurvitch's rule (26) for the Pd/SiO$_2$ catalysts. The surface area obtained by the DRK method provides higher values than those derived from the BET equation, but the trends are the same. It should be kept in mind that the validity of the DRK method is restricted to microporous systems; therefore the more appropriate surface values for these samples prepared at pH 3 are those calculated by this method.

Hydrogen chemisorption isotherms at 343 K were carried out in order to estimate palladium dispersion. For calculation of the metal particle size a stoichiometry of adsorption H/Pd$_s$ = 1 was assumed and the particle size was evaluated from the equation $d = 5/S\rho$, where S is the metal surface area and ρ is the metal density. The obtained values for fresh samples are compared with those evaluated from TEM results and they are compiled in Table 2. Even though the values obtained by both methods are different, the trends observed in the particle size values are the same. Taking into account that the values of pore diameters given in Table 1 represent an average pore size and, considering that sol-gel catalysts obtained at pH 3 are essentially

TABLE 1

Specific Surface Area, Pore Volume, and Average Pore Diameter of 0.5 wt% Pd/SiO$_2$ Catalysts

Catalysts	S$_{\text{BET}}$ (m^{2}g^{-1})	S$_{\text{DRK}}$ (m^{2}g^{-1})	Pore volume (cm^{3}g^{-1})	Average pore diameter (nm)	
				BET	DRK
Pd/SiO$_2$ (SG)-A	285	436	0.154	2.2	1.4
Pd/SiO$_2$ (SG)-B	388	548	0.206	2.2	1.5
Pd/SiO$_2$ (SG)-C	698	869	0.604	3.6	2.8
Pd/SiO$_2$ (SG)-D	169	244	0.210	5.0	3.4
Pd(I)/SiO$_2$-A	147	208	0.072	2.0	1.4
Pd(I)/SiO$_2$-B	429	659	0.234	2.2	1.4
Pd(I)/SiO$_2$-C	524	722	0.525	4.0	2.9
Pd(I)/SiO$_2$-D	290	415	0.441	6.0	4.3

Note. A, pH = 3, HCl; B, pH = 3, H$_2$SO$_4$; C, pH = 5, CH$_3$COOH; D, pH = 9, NH$_4$OH.

TABLE 2

Metal Particle Size for 0.5 wt% Pd/SiO$_2$ Catalysts

Catalysts	Particle size *d* (nm)	
	QH$_2$	TEM
Pd/SiO$_2$ (SG)-A	2.5	3.2
Pd/SiO$_2$ (SG)-B	3.0	3.2
Pd/SiO$_2$ (SG)-C	2.0	2.0
Pd/SiO$_2$ (SG)-D	3.3	3.5
Pd(I)/SiO$_2$-A	2.5	3.0
Pd(I)/SiO$_2$-B	13	10
Pd(I)/SiO$_2$-C	1.6	2.0
Pd(I)/SiO$_2$-D	3.1	3.5

Note. A, pH = 3, HCl; B, pH = 3, H$_2$SO$_4$; C, pH = 5, CH$_3$COOH; D, pH = 9, NH$_4$OH.

microporous, it can reasonably be inferred that in these catalysts the metal crystallites may remain trapped in the pore structure, making the migration of these particles difficult. At higher pH values no good relationships between average pore diameter and metal particle size were observed. This fact does not mean that metal particles are not trapped in small pores, because in these solids an increase in the average pore diameter is due to a higher contribution of meso- and macropores, but a significant fraction of small pores still remain in the pore structure. Even though the catalysts prepared by impregnation have particle size values comparable to those obtained from the sol-gel methods, with the exception of the sample prepared at pH 3, H_2SO_4, it may be expected that the metal crystallites should not be trapped in the pore structure, considering the diffusion limitation of the organometallic precursor to access these small pores and, therefore, the migration of the metal particles under sintering conditions are more likely. Figure 2 shows a TEM micrograph for one of the Pd/SiO_2 catalysts (sample A) in which a narrow particle size distribution can be observed. Similar micrographs were obtained for all catalysts.

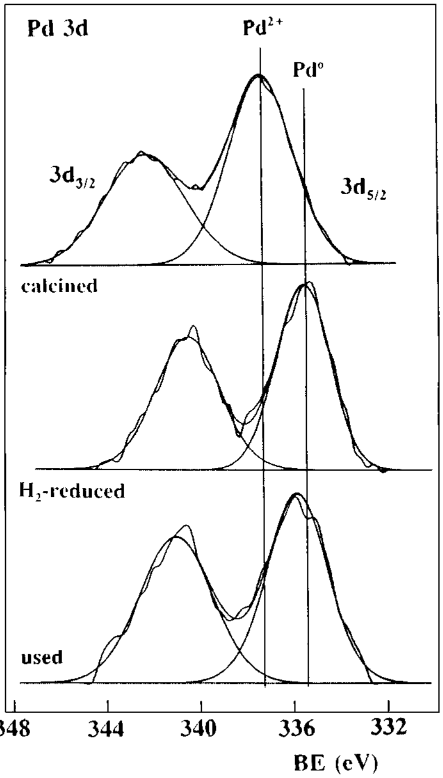

FIG. 3. XPS spectra for Pd-SiO_2 (I)-A catalysts: (a) calcined sample; (b) H_2-reduced sample; (c) after combustion cycle (used).

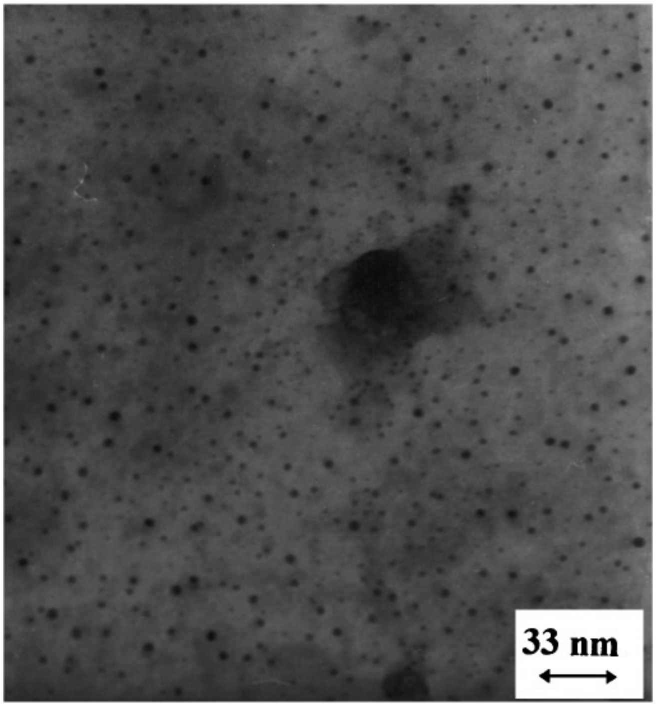

FIG. 2. TEM micrograph of Pd-SiO_2 (SG) catalysts obtained at pH = 3-HCl.

The chemical state of Pd and the changes of metal exposure at the catalyst surface for all catalysts have been revealed by XPS. The Pd $3d_{5/2}$ core level spectra of a representative Pd/SiO_2 catalyst in its calcined, H_2-reduced, and used forms are displayed in Fig. 3. The calcined catalyst shows the Pd $3d_{5/2}$ peak at a B.E. of 337.1 eV, which is typical of PdO species (18–20). Reduction of the catalyst shifted the Pd $3d_{5/2}$ component to 335.2 eV and its full width at half maximum (FWHM) of the peak decreased slightly. The comparison of the B.E. values of Pd $3d_{5/2}$ core level of several supported-palladium catalysts indicate that B.E. values close to 335.2 eV are responsible for Pd° species (27–31). Upon exposure the reduced catalyst within the pretreatment chamber of the spectrometer to a mixture $CH_4 : O_2 = 1 : 2$ molar ratio at 773 K for 2 h, the B.E. of the Pd $3d_{5/2}$ shifted to 336.0 eV while its FWHM increased and reached a value similar to that of the calcined counterpart, from which it can be concluded that the palladium became partially oxidized ($Pd_{\delta+}$). Similar trends were observed in all the studied catalysts. Table 3 summarizes the binding energies of Pd $3d_{5/2}$ and Pd/Si surface ratios. A drastic decrease in the Pd/Si surface ratio can be observed by comparing the calcined and reduced samples for the catalysts obtained from the impregnation method. This is an expected result because it is widely recognized that Pd is resistant to sintering in an oxygen atmosphere, but substantial sintering in a hydrogen atmosphere due to mobile hydrides usually occurs. Conversely, in catalysts prepared by the sol-gel methods, the Pd/Si ratio remains almost constant. This behaviour can be explained considering that in the catalysts prepared by the sol-gel method the metal migration is strongly limited, because it is placed into very small pores of the support structure. Additionally, the Pd/Si ratios

TABLE 3

Binding Energies (eV) of Core Electrons of Pd 3d$_{5/2}$ and Surface Atomic Ratios of Calcined (O), Reduced (R), and Used (U) 0.5 wt% Pd/SiO$_2$ Catalysts

Catalysts	B.E. (eV) (O)	B.E. (eV) (U)	Pd/Si (O)	Pd/Si (R)	Pd/Si (U)
Pd/SiO$_2$ (SG)-A	337.1	335.8	0.008	0.007	0.006
Pd/SiO$_2$ (SG)-B	336.9	336.0	0.010	0.10	0.010
Pd/SiO$_2$ (SG)-C	336.9	336.2	0.006	0.005	0.004
Pd/SiO$_2$ (SG)-D	336.9	335.9	0.004	0.004	0.003
Pd(I)/SiO$_2$-A	337.1	336.0	0.287	0.085	0.066
Pd(I)/SiO$_2$-B	336.9	335.9	0.053	0.023	0.017
Pd(I)/SiO$_2$-C	336.9	336.0	0.013	0.010	0.006
Pd(I)/SiO$_2$-D	336.8	336.2	0.005	0.004	0.002

Note. A, pH = 3, HCl; B, pH = 3, H$_2$SO$_4$; C, pH = 5, CH$_3$COOH; D, pH = 9, NH$_4$OH.

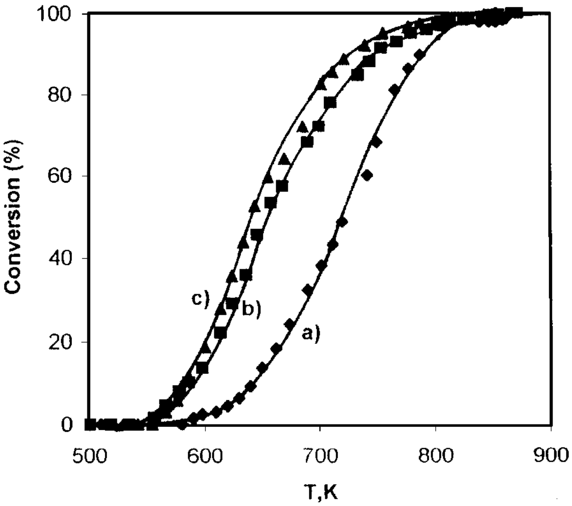

FIG. 4. Activity data of methane oxidation for Pd-SiO$_2$ (SG)-A catalysts: (a) calcined sample; (b) reduced sample; (c) after combustion cycle (used).

are much higher in those samples obtained by impregnation than those prepared by sol-gel methods, due to the fact that in these the metal is buried in the support; consequently higher resistance to sintering may be expected (20). Small amounts of carbonaceous compounds were detected in the fresh reduced samples which correspond to residues of the organometallic precursor. A slight increase in the C/Pd ratios was detected in the samples used, compared with the reduced ones, indicating that carbon deposition occurs upon catalytic reaction. This may explain the observed decreases in the Pd/Si ratios in the catalysts after the catalytic reaction. Additionally, sulfated species were detected in samples detected by gelation using H$_2$SO$_4$ as the hydrolysis catalyst.

Figure 4 shows activity data for methane oxidation as a function of the reaction temperature up to complete combustion for one of the representative catalysts. Typical sigmoidal curves can be observed. The reaction starts at about 550 K; then the conversion increases drastically as the temperature increases and the complete conversion is reached at temperatures lower than 800 K. Up to 30% of conversion, only CO$_2$ and H$_2$O were the observed products. At higher conversion levels (>60%), the selectivity to CO$_2$ decreases to 95%, CO being the other product. At conversion close to 100% traces of H$_2$ and C$_2$H$_6$ were also detected. The calcined sample is active in methane oxidation but its activity is lower than the reduced catalyst. Moreover, when a new catalytic cycle is carried out on the used catalyst, the second cycle exhibits the same behaviour; however, an increase in the activity is produced. This feature has been reported previously for Pd-supported catalysts (32, 33) and it has been attributed to a slight oxidation of the metal clusters leading to more active species than the reduced ones. Similar trends are observed for all the studied catalysts, but they show differences in the conversion levels at each temperature. Table 4 summarizes activity results for the studied Pd/SiO$_2$ catalysts.

The ignition temperature, defined as the temperature required to obtain a 50% conversion, presents significant differences in the series of studied Pd/SiO$_2$ catalysts. The

TABLE 4

Catalytic Activity of Pd/SiO$_2$ Catalysts in the Methane Combustion

Catalysts	Ignition temp. (K) 1°cycle	Ignition temp. (K) 2°cycle	Ignition temp. (K) 3°cycle	TOF $*$ 10^2 (s^{-1}) at 600 K	TOF $*$ 10^2 (s^{-1}) at 623 K
Pd/SiO$_2$ (SG)-A	720	650	642	0.81	2.43
Pd/SiO$_2$ (SG)-B	715	680	665	0.74	2.23
Pd/SiO$_2$ (SG)-C	630	620	615	2.20	3.30
Pd/SiO$_2$ (SG)-D	710	700	695	1.23	2.21
Pd(I)/SiO$_2$-A	645	635	628	2.47	4.12
Pd(I)/SiO$_2$-B	730	710	700	2.31	4.60
Pd(I)/SiO$_2$-C	590	580	575	3.41	4.23
Pd(I)/SiO$_2$-D	665	650	632	3.45	4.22

Note. A, pH = 3, HCl; B, pH = 3, H$_2$SO$_4$; C, pH = 5, CH$_3$COOH; D, pH = 9, NH$_4$OH.

solids obtained by gelation at pH 5 either prepared by sol-gel or impregnation have the better activity. On the other hand, the turnover frequency (TOF) at a given temperature, 600 or 623 K, evaluated from hydrogen chemisorption on fresh samples, reveals that for each series of catalysts the TOF values are almost constant and are not affected by the particle size. In agreement with Dalla Betta *et al.* (13) and Cullis *et al.* (14), the TOF were estimated during the first cycle of combustion using the metallic area evaluated from hydrogen adsorption. Even though it is recognized that the active phase may require the presence of $Pd_{\delta+}$ species, these species are mainly formed during combustion, essentially at higher temperatures. Therefore, during the first cycle and at low conversion level, a palladium species exists as Pd°, so the calculation of the TOF makes sense. However, the activity per site in the catalysts prepared by impregnation is much higher (60–300%) than their sol-gel counterparts. This behaviour may be attributed to a different location of the Pd particles. Thus, in Pd/SiO_2 (SG), the metal particles may partially remain in the porous structure, limiting the surface reaction, whereas in those prepared by impregnation of the support, due to the molecular size of the organometallic precursor, it is likely that the metal particles are not trapped in the microporous structure and, therefore, access of the reactant molecule to the active sites is easier.

CONCLUSIONS

The influence of different variables of preparation of Pd/SiO_2 catalysts on their surface and catalytic properties was studied. It was found that the pH of gelation, modifies strongly the porosity and specific surface area, the contribution of micropores being higher at lower pH. The comparison of sol-gel and impregnation methods reveal that the Pd particles become trapped when the former procedure is used, whereas they are located in the mesopore and macropore structure in the impregnated catalysts. The activity in the combustion of methane depends mainly on the metal location and the oxidation state of the Pd species. The presence of Pd crystals in meso- or macropores explains the higher turnover frequency of the catalysts prepared by impregnation. Additionally, it was found that $Pd_{\delta+}$ species seem to be responsible for the improvement in catalytic activity. No effect of metal dispersion was detected.

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