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Comparative Study by Infrared Spectroscopy and Microcalorimetry of the CO Adsorption over Supported Palladium Catalysts

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The adsorption of CO on Al_2O_3, ZrO_2, ZrO_2−SiO_2, and ZrO_2−La_2O_3 supported Pd catalysts was studied by adsorption microcalorimetry and infrared (IR) spectroscopy. Some interesting and new correlations between the results of microcalorimetry and IR spectroscopy have been found. The CO is adsorbed on palladium catalysts in three different modes: multibonded (3-fold), bridged (2-fold), both on Pd (111) and (100) planes, and linear (1-fold) adsorbed species. The corresponding differential adsorption heats lie in the field of high (210−170 kJ/mol), medium (140−120 kJ/mol), and low (95−60 kJ/mol) values, respectively. The nature of the support, the reduction temperature, and the pretreatment conditions affect the surface structure of the Pd catalysts, resulting in variations in the site energy distribution, i.e., changes in the fraction of sites adsorbing CO with specific heats of adsorption. Moreover, the CeO_2 promoter addition weakens the adsorption strength of CO on palladium. Based on the exposed results, a correctness factor, which considers the percentages of various CO adsorption states, must be introduced when one calculates the Pd dispersion using CO adsorption data.

1. Introduction

Supported Pd catalysts were found to be the most active and promising catalysts for methane combustion, and therefore they have received much attention in the past decades.[1−5] In spite of the intensive research of the system, there is still a lack of agreement on questions such as the mechanism of the catalytic process, the structure-sensitive character of the reaction, or the nature of the most active catalyst. These differences in conclusions arise from the strong dependency of the palladium catalyst activity on the support, the pretreatment, and the reaction conditions.[4]

To better understand the catalytic nature of supported Pd catalysts an in-depth study of their surface chemistry would be necessary. Among many techniques available, adsorption microcalorimetry and infrared spectroscopy (FTIR) are very powerful two. The former can provide information about the energy of interaction of reactive molecules with the surface of the catalyst, which is a parameter related with the surface structure of the catalyst,[6,7] while the latter, combined with adsorption of probe molecules, e.g., CO, can give useful information about the surface state and active sites of a catalyst. There have been some studies on determinations of calorimetric heat of CO adsorption over supported palladium[8−13] and many studies on infrared spectroscopy of adsorbed CO;[14−16] however, few of them studied the Pd catalysts using microcalorimetry and IR comparatively.

In this paper, supported Pd catalysts were studied combining adsorption microcalorimetry and infrared spectroscopy of adsorbed CO. It was found that the results obtained by the two techniques are complementary and provide evidence of the surface structure of the Pd catalysts. The influence of pretreatment conditions, nature of the support, and CeO_2 promoter addition on the energetic and adsorption modes of CO on Pd supported catalysts will be discussed.

2. Experimental Section

2.1. Catalyst Preparation. The catalysts were prepared by incipient wetness impregnation of the supports with aqueous solution of $Pd(NO_3)_2$. The catalysts were dried overnight at 393 K after impregnation, and then calcined in air at 773 K for 2 h. The surface area of the supports, Al_2O_3 (Condea), ZrO_2 (MEL zirconium hydroxide), ZrO_2−SiO_2 (MEL zirconium hydroxide stabilized with 3.5% SiO_2), and ZrO_2−La_2O_3 (MEL zirconium hydroxide stabilized with 6% La_2O_3), were 379, 20, 75, and 41 m^2/g, respectively, after calcination in air at 973 K for 4 h. The palladium content of the as-prepared catalysts, Pd/Al_2O_3, Pd/

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ZrO_2, Pd/ZrO_2–SiO_2, and Pd/ZrO_2–La_2O_3 is near 1 wt %. These catalysts were in part described elsewhere.[17]

For Ce-promoted samples, the Ce was first added to the support by incipient impregnation with solutions of cerium nitrate. After drying overnight at 393 K and calcining in air at 773 K for 2 h, the obtained CeO_2/supports were impregnated with aqueous Pd-$(NO_3)_2$ solution. Then the same drying and calcination procedures as described above were carried out. The Ce content in the samples is close to 5 wt %.

2.2. FTIR Adsorption Experiments. The calcined samples were pressed into self-supported wafers, ca. 10 mg/cm². A quartz IR cell with CaF_2 windows was used for the IR experiments. The temperature was increased at 10 K/min up to 773 K in a H_2/N_2 (1:1) mixture flowing at 80 mL/min, and held at that temperature for 2 h. Once the catalyst was purged with N_2 at the same temperature for 1 h and cooled to room temperature in the N_2 flow, a spectrum of the clean sample was collected. Subsequently, 0.8 ml of CO was pulsed into the IR cell, and the spectrum of adsorbed CO was recorded after 15 min. Then, the reaction mixture, $CH_4/O_2/N_2$ ($CH_4/O_2 = 1:4$, 5% CH_4), was switched on. After reacting at 773 K for 0.5 h, the catalyst was cooled to room temperature and the same CO adsorption procedure was performed. All the spectra were collected at room temperature on a Fourier transform infrared spectrometer (Nicolet 5 ZDX) equipped with a liquid nitrogen cooled MCT (mercury–cadmium–telluride) detector at a resolution of 4 cm^{-1} and 128 scans in the region 4000–1000 cm^{-1}. The results given herein are difference spectra with the spectrum of the clean sample before adsorption as the background.

2.3. Microcalorimetry of CO Adsorption. The apparatus has been described in detail elsewhere.[18–20] In brief, the heats of CO chemisorption were measured in a differential heat-flow microcalorimeter of the Tian-Calvet type (Setaram C-80 II) operated isothermally at 330 K. For most experiments, the catalysts were first in situ reduced under hydrogen flow at a given temperature for 2 h, outgassed overnight at 673 K, and cooled to 330 K. Subsequently, successive doses of CO were introduced onto the catalyst. Both the calorimetric and volumetric data were automatically stored and analyzed by microcomputer processing. In some cases, the mixture CH_4/O_2, balance N_2, was admitted into the cell and the reaction was performed at 773 K for 2 h. After reaction, the samples were outgassed at 673 K overnight to remove adsorbed species from the surface. Subsequently, the samples were cooled to 330 K and the above CO adsorption procedure was conducted. The metallic dispersion of reduced samples was obtained from the total amount of CO uptake at the monolayer. This latter is covered when the heat evolved falls in the physisorption field (40 kJ/mol).

3. Results and Discussion

3.1. Influence of Pretreatment Conditions. Figure 1 shows the differential heats of CO adsorption at 330 K as a function of surface coverage for Pd/Al_2O_3 treated at various conditions. The carbon monoxide coverage is determined as the ratio between the adsorbed amount at a given point and the monolayer uptake of the sample. This procedure facilitates comparison of catalysts with different metal loadings and dispersions. Comparison of the curves reveals that three plateaus with characteristic values at the high, medium, and low regions of adsorption differential heat can be clearly observed. However, the energetic distribution of surface CO adsorption sites is a function of the sample pretreatment. It can be seen that the Pd/Al_2O_3 sample reduced at 673 K exhibits a initial differential heat of CO adsorption of 200 kJ/mol, and this value remains constant up to $\theta = 0.4$. Then, the adsorption
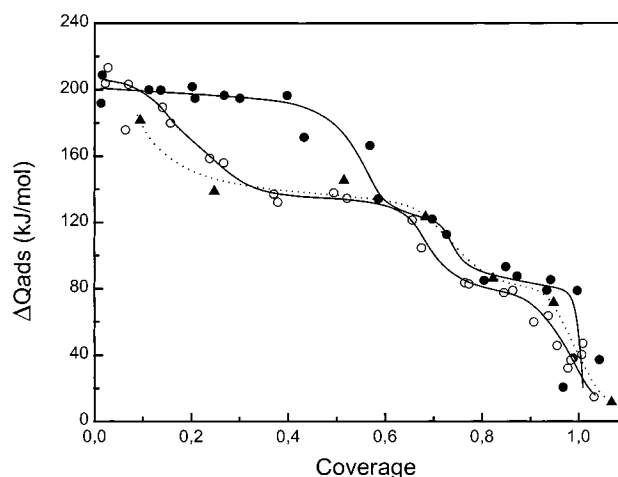
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Figure 1. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pd/Al_2O_3: (●) reduced at 673 K, (○) reduced at 773 K, and (▲) reaction at 773 K.

heat decreases with further increase of CO coverage and attains a constant value, 130 kJ/mol, in the region of $\theta = 0.6$–0.7. At coverages of 0.8–1.0, the adsorption heat resembles a stable value of ca. 90 kJ/mol. When the sample was reduced at 773 K, the heats of adsorption corresponding to the three plateaus do not change very much, but the corresponding ranges of coverages are modified suggesting that the fraction of sites adsorbing CO with a specific heat of adsorption has changed. Thus, the fraction of medium-energy surface sites for CO adsorption is strongly increased mainly at the expense of the high-energy surface sites. Moreover, the calorimetric curves show that the site energy distribution obtained over the catalyst reduced at 773 K does not largely change when subsequently the catalyst is subjected to methane combustion reaction at 773 K. The distinct plateaus of the calorimetric curves may correspond to either different type of surface adsorption sites and/or of CO adsorption modes.[6,7]

It is noteworthy that the above values of initial heat of CO adsorption on the Pd/Al_2O_3 catalyst treated under different conditions are much higher than others reported before. Chou and Vannice[9] using a modified differential scanning calorimeter (DSC) reported adsorption heats between 81.7 and 149.2 kJ/mol for CO on Pd/Al_2O_3 with Pd loadings of 0.36–2.33 wt %. Dropsch and Baerns[13] reported an initial heat of CO adsorption on 2 wt % Pd/Al_2O_3 of 172 kJ/mol, and this value drops to 99 kJ/mol when the Pd loading increases to 10 wt %. The influence of Pd loading on CO adsorption energetic was explained in terms of particle size and/or surface structure of Pd crystallites. For unsupported Pd surfaces, the initial isosteric heat of adsorption varies from 142 kJ/mol for Pd (111) to 167 kJ/mol for Pd (110),[21] while the reported values of initial adsorption heat for other planes, like the (100), (210), (112), (311), and (331), are between those of the (111) and (110) planes.[21–23] Also, similar values for the heats of CO adsorption on Pd (111) and on (100) planes were reported.[24] Therefore, it is unreasonable to attribute the three plateaus of differential adsorption heat to CO adsorbed on different planes of palladium, in spite of the fact that the surface of alumina supported Pd catalyst is

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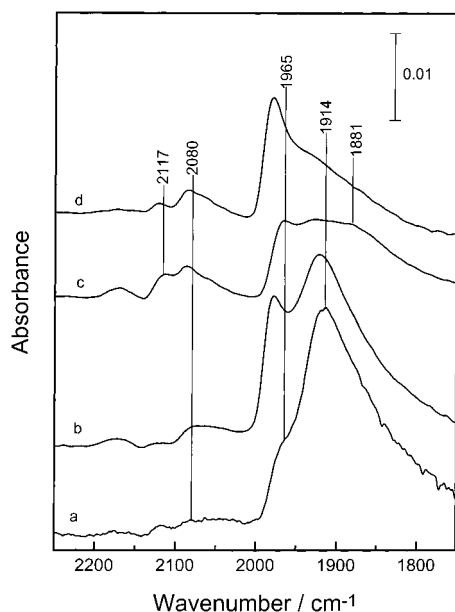
Figure 2. IR spectra of CO adsorbed on Pd/Al$_2$O$_3$ treated at various conditions: (a) reduced at 673 K, (b) reduced at 773 K, (c) reaction at room temperature, and (d) reaction at 773 K.

Figure 3. IR spectra of CO adsorbed on Pd/Al$_2$O$_3$ reduced at 773 K as a function of purging temperature: (a) room temperature, (b) 373 K, and (c) 473 K.

polycrystalline and does contain various planes with low index, such as Pd (100) and Pd (111).[15,16]

Figure 2 shows the IR spectra of CO adsorbed on Pd/Al$_2$O$_3$ treated at different conditions. When the catalyst was reduced at 673 K, three peaks at 2080 (very weak), 1965, and 1914 cm^{-1} appear in the region of 2100–1800 cm^{-1}, which can be attributed to linearly adsorbed CO, and bridge-bonded CO on Pd (100) and Pd (111) planes, respectively.[15,16,25] The increase in the reduction temperature to 773 K causes that the bands attributed to bridged CO species shift to higher frequencies, 1978 and 1921 cm^{-1}, suggesting a sintering of the palladium particles. Moreover, the intensity of the 1978 cm^{-1} is enhanced with respect to the 1921 cm^{-1} band. This fact indicates that the population of (111) and (100) planes on the palladium crystallites has changed, although in both cases the Pd (111) plane is predominant on the reduced samples. Previous reports demonstrated that at room temperature and above, CO adsorbs on Pd single crystals mainly bridge-bonded. Only on the Pd (111) surface does CO adsorb initially on 3-fold sites, up to a coverage of 1/3, and subsequently at saturation coverage ($\theta > 0.5$) the CO molecules are bridge-bonded.[26] Besides the above-described peaks and according with the literature, another band at ca. 1880 cm^{-1} due to multibonded CO species exists in spectra a and b of Figure 2. This latter is overlapped with the 1921 cm^{-1} band, but it can be clearly seen when the reduced sample with adsorbed CO is degassed at increasing higher temperatures, i.e., at low CO coverages (Figure 3) or when CO is adsorbed on the sample exposed to reaction mixture, CH$_4$/O$_2$/N$_2$, at room temperature (Figure 2c). Moreover, after reacting at 773 K, the CO species adsorbed on Pd (111) planes are strongly diminished while the bridged CO species on Pd (100) planes are preferentially formed. Therefore, the IR spectra allow us to make distinction between various CO species adsorbed on the different planes present at the palladium surface.

Based on the IR results (Figures 2 and 3) the energy distribution showed by the calorimetric curves (Figure 1)
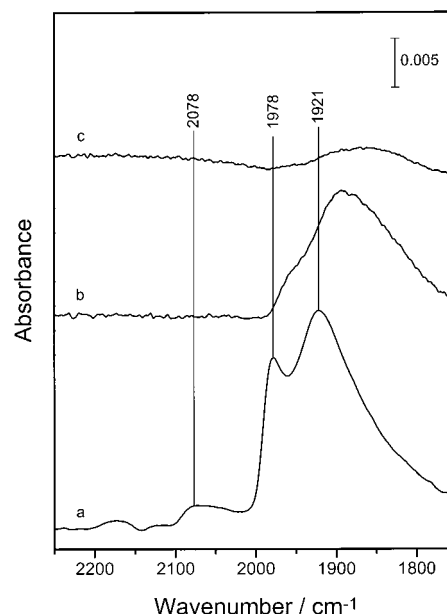
can be interpreted as follows. Differential adsorption heats (ΔQ_{ads}) at the high-value region (200 kJ/mol) can be attributed to the formation of multibonded CO on 3-fold site of Pd (111) planes, which results in high adsorption strength of CO on Pd, and therefore, originates high initial adsorption heat. The lower ΔQ_{ads} (140 kJ/mol) can be attributed to the formation of bridged CO, both on Pd (100) and Pd (111) planes, while low ΔQ_{ads} (90 kJ/mol) can be ascribed to the formation of linearly adsorbed CO. Thus, the depletion in the surface population of multibonded CO species and enhancement of the bridged CO species caused by the increase in the reduction temperature, as seen in the IR spectra of Figure 2, is consistent with the narrowing of the plateau at high ΔQ_{ads} (200 kJ/mol) and the enlargement of that corresponding to medium ΔQ_{ads} (140 kJ/mol) (Figure 1). Consequently, it can be inferred that the differences in site energy distribution observed over the Pd/Al$_2$O$_3$ catalyst submitted to distinct pretreatments (Figure 1) were caused by a change in the fraction of sites adsorbing CO with specific heats of adsorption. Our assignments are consistent with TPD results[13,27] which showed that bridged CO is more stable than the linearly adsorbed one and desorbs at much higher temperatures.

Figure 4 gives the differential adsorption heat versus the CO coverage and Figure 5 displays the IR spectra of CO on Pd/ZrO$_2$ treated under various conditions. For the sample reduced at 673 K, the initial heat of CO adsorption of 190 kJ/mol decreases to a large plateau at 175 kJ/mol from $\theta = 0.1$ to 0.4, before decreasing to a second plateau at 120 kJ/mol up to $\theta = 0.85$. At this point the heat drops abruptly to 20 kJ/mol. When the reduction temperature is increased to 773 K, the amount of CO adsorbed decreases dramatically (see Table 1) and although the initial CO adsorption heat is similar, the dependence of the heat of adsorption on coverage is significantly different. So, the adsorption heat decreased from 196 to 60 kJ/mol at $\theta = 0.25$ and remained nearly constant for the rest of the surface coverage. These facts indicate the predominant exposition on the 773 K reduced sample of surface sites adsorbing CO in a linear mode. When the 773 K reduced

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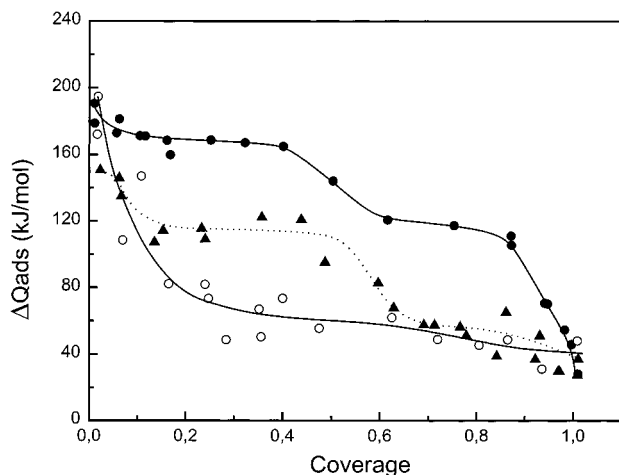
Figure 4. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pd/ZrO$_2$: ($\bullet$) reduced at 673 K, ($\bigcirc$) reduced at 773 K, and ($\blacktriangle$) reaction at 773 K.

Figure 6. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pd/ZrO$_2$−SiO$_2$: ($\bullet$) reduced at 673 K, ($\bigcirc$) reduced at 773 K, and ($\blacktriangle$) reaction at 773 K.
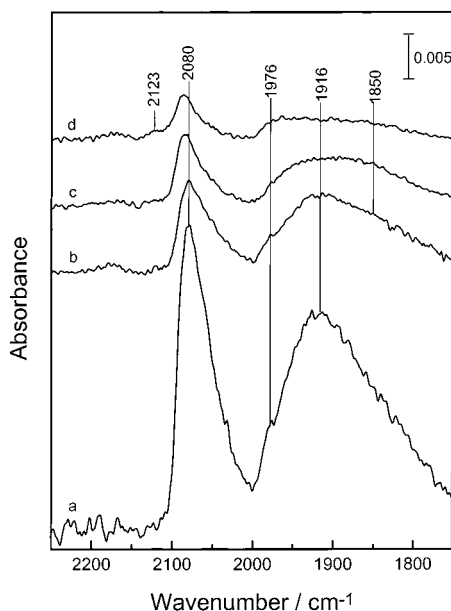

Figure 5. IR spectra of CO adsorbed on Pd/ZrO$_2$ treated at various conditions: (a) reduced at 673 K, (b) reduced at 773 K, (c) reaction at room temperature, and (d) reaction at 773 K.

Table 1: Initial CO Adsorption Heat ($\Delta Q_{ads,0}$), CO Adsorption Amount and Pd Dispersion of Supported Pd Catalysts Reduced at 673 and 773 K

	reduced at 673 K			reduced at 773 K		
sample	ΔQ_{ads} (kJ/mol)	N_{ads} (μmol/g)	D (%)	ΔQ_{ads} (kJ/mol)	N_{ads} (μmol/g)	D (%)
Pd/Al$_2$O$_3$	202	19	20.2	210	16	17.0
Pd−Ce/Al$_2$O$_3$	200	21	22.3	170	17.1	18.2
Pd/ZrO$_2$	190	27	28.7	196	12	12.8
Pd−Ce/ZrO$_2$	141	19	20.2	170	17	18.1
Pd/ZrO$_2$−SiO$_2$	168	11.5	12.2	205	8.5	9.0
Pd−Ce/ZrO$_2$−SiO$_2$				172	10.6	11.3
Pd/ZrO$_2$−La$_2$O$_3$	171	14	14.9	168	7.5	8.0
Pd−Ce/ZrO$_2$−La$_2$O$_3$				145	20.5	21.8

sample is exposed to reaction mixture (CH$_4$ + O$_2$) at 773 K, the calorimetric adsorption heat curve (Figure 4) shows the appearance of two plateaus at the field of medium (120 kJ/mol) and low (60 kJ/mol) differential adsorption heats which can be assigned to bridge and linear CO adsorption, respectively. This finding suggests that the surface sites responsible of the bridged CO adsorption are again replaced on the sample during methane
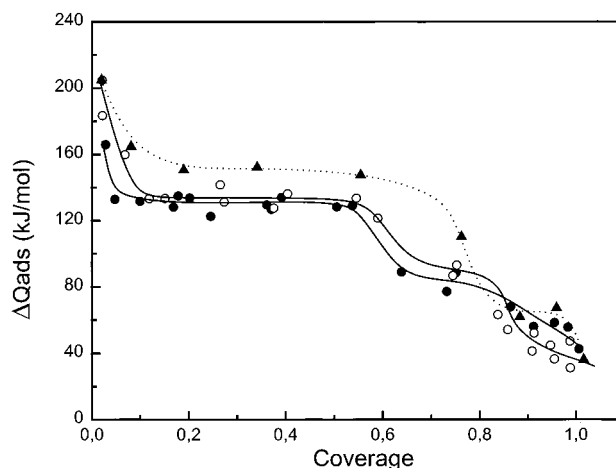
combustion reaction. The IR spectra of CO adsorbed on Pd/ZrO$_2$ catalyst (Figure 5) corroborate these points. For the reduced catalyst it can be seen the only presence of CO species adsorbed on Pd (111) planes and, also, the band intensity of the linearly adsorbed CO is higher than that of bridged ones, which is different from that found for Pd/Al$_2$O$_3$ (Figure 2) but is consistent with the calorimetric results (Figure 4). After reacting at 773 K in the CH$_4$ + O$_2$ mixture (Figure 5d), the band due to adsorbed CO on Pd (100) planes increases in intensity, while the bands due to adsorbed CO on Pd (111) planes decrease.

Figure 6 shows the microcalorimetry results of CO adsorbed on Pd/ZrO$_2$−SiO$_2$. It can be seen that there is a rapid decrease of the initial ΔQ_{ads} at very low coverages to $\theta = 0.05−0.1$, as well as two plateaus at the field of medium and low values of differential adsorption heats. The increase of the reduction temperature did not cause much difference in the adsorption heat values and in the site energy distribution. The IR spectra of CO adsorbed on Pd/ZrO$_2$−SiO$_2$ reduced at 673 and 773 K are also very similar (see Figures 7a,b). The IR spectra allow the assignation of the three zones of CO adsorption heats showed in the calorimetric curves (Figure 6) to the formation of multibonded, bridged, and linearly adsorbed CO, respectively. After the catalyst is treated under reaction conditions at 773 K, Pd (100) plane becomes predominant on the catalyst; therefore, an enlargement of the plateau at medium adsorption heat values (150 kJ/mol), assigned to CO adsorption in a bridged mode (Figure 7), can be observed.

3.2. Influence of the Support. To better determine the support effects on the modes and heats of CO adsorption over palladium catalysts, the microcalorimetry and IR results of CO adsorbed on Pd/Al$_2$O$_3$, Pd/ZrO$_2$, Pd/ZrO$_2$−SiO$_2$, and Pd/ZrO$_2$−La$_2$O$_3$ are illustrated in Figures 8 and 9. It can be clearly seen (Figure 9) that, independent of the support, the CO is adsorbed on palladium in three different modes: multibonded CO (ca. 1850 cm^{-1}), bridged CO (ca. 1920 and ca. 1980 cm^{-1}), and linearly adsorbed CO (ca. 2080 cm^{-1}). These adsorption modes give differential adsorption heats in three fields: high (210−170 kJ/mol), medium (140−120 kJ/mol), and low (95−60 kJ/mol), respectively. However, the energetic distribution of adsorption sites on the samples is a function of the support and also of the reduction temperature; i.e., both the support and the reduction temperature give rise to changes in the fraction of sites adsorbing CO with specific heats. The Al$_2$O$_3$ and ZrO$_2$ supported Pd catalysts are affected
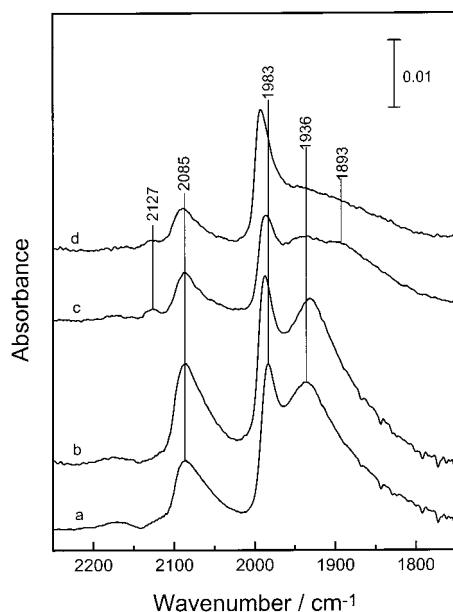
Figure 7. IR spectra of CO adsorbed on Pd/ZrO_2-SiO_2 treated at various conditions: (a) reduced at 673 K, (b) reduced at 773 K, (c) reaction at room temperature, and (d) reaction at 773 K.
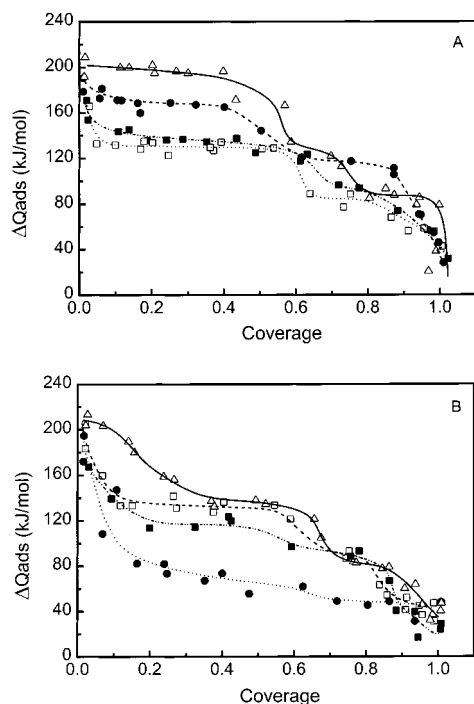

Figure 8. Differential heats of CO adsorption at 330 K as a function of surface coverage for Pd catalysts supported on ($\triangle$) Al_2O_3, ($\bullet$) ZrO_2, ($\square$) ZrO_2-SiO_2, and ($\blacksquare$) $ZrO_2-La_2O_3$ reduced at 673 K (a) and 773 K (b).

significantly by an increase of reduction temperature from 673 to 773 K, while the ZrO_2-SiO_2 and $ZrO_2-La_2O_3$ supported Pd are less affected. Dropsch and Baerns[13] studied the influence of support materials on CO adsorption heat. They found that Pd supported on TiO_2 or Al_2O_3 supports is characterized by an increased sensitivity of CO adsorption to reduction temperature, although the contrary is found on Pd supported on SiO_2.

It is worth noting the different sensitivity to reduction temperature that zirconia-supported palladium samples have depending on the presence or absence of stabilizer in the zirconia support. At this point, it should be noted that the crystallographic structure of the ZrO_2 support is
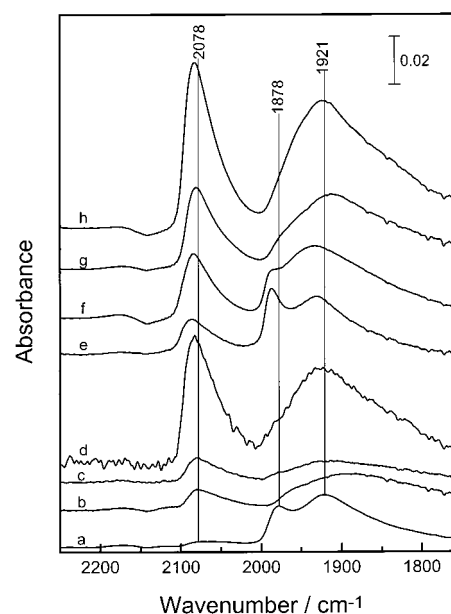

Figure 9. IR spectra of CO adsorbed on different catalysts reduced at 773 K: (a) Pd/Al_2O_3, (b) $Pd-Ce/Al_2O_3$, (c) Pd/ZrO_2, (d) $Pd-Ce/ZrO_2$, (e) Pd/ZrO_2-SiO_2, (f) $Pd-Ce/ZrO_2-SiO_2$, (g) $Pd/ZrO_2-La_2O_3$, and (h) $Pd-Ce/ZrO_2-La_2O_3$.

monoclinic, while ZrO_2-SiO_2 and $ZrO_2-La_2O_3$ are tetragonal.[20] Comparison of the ΔQ_{ads} profiles and IR spectra of CO adsorbed on palladium supported on zirconia (Pd/ ZrO_2) and on palladium supported on stabilized zirconia (Pd/ZrO_2-SiO_2 and $Pd/ZrO_2-La_2O_3$) reduced at 673 K already reveals differences in the surface morphology of the palladium crystallites. This latter is likely induced by the different crystallographic structure of the support. In a similar way, the differential feature of Pd/ZrO_2 reduced at 773 K, i.e., predominant exposition of sites adsorbing CO with low heat, may be partially due to the occurrence of a kind of interaction of Pd with the monoclinic ZrO_2, which does not occur with stabilized zirconia of tetragonal structure. The interaction of some noble metals, such as Ru, Rh, and Pt, with ZrO_2 when treated with H_2 at high temperature has been reported before.[28,29] The formation of Zr-O-Rh entities formed to such an extent that the metal particle is partly covered by the support has been proposed.[29] From our results, the CO adsorption amount on Pd/ZrO_2 decreases dramatically with the increase of reduction temperature (Table 1); this fact indicates the presence of Pd-Zr interaction. It can be deduced that some sites available for CO adsorption may be occupied by ZrO_2, and this weakens the strength of CO adsorption. Further studies are in progress to better understand the interaction of Pd with ZrO_2 samples of different structure features.

3.3. Influence of the Ce Addition. The catalytic effects of Ce addition to Pd catalysts for methane combustion have been investigated extensively. It has been found that cerium oxide promotes the activity of the catalyst,[30] and increases its stability against thermal deactivation for CH_4 combustion.[31] To understand the effect of Ce on the surface properties of Pd catalysts, the changes over the CO adsorption states on Ce-containing catalysts were

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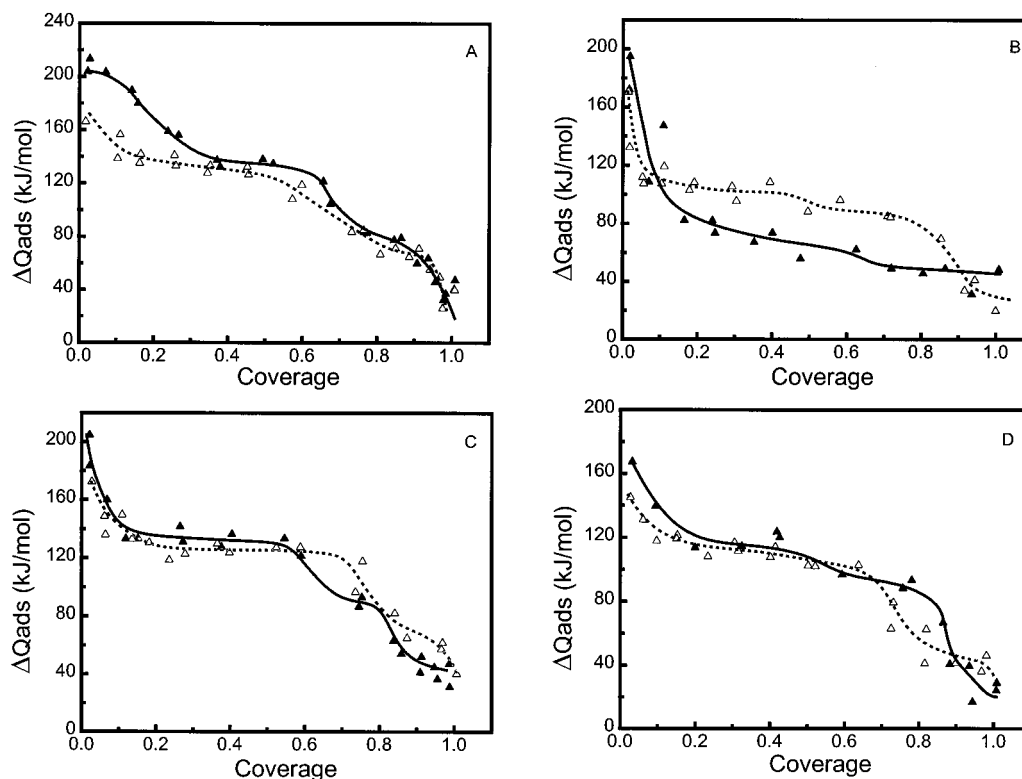
Figure 10. Differential heats of CO adsorption at 330 K as a function of surface coverage for 773 K reduced (▲) Pd-only and (△) Pd−Ce catalysts supported on (a) Al_2O_3, (b) ZrO_2, (c) ZrO_2−SiO_2, and (d) ZrO_2−La_2O_3.

studied by microcalorimetry and IR. The differential CO adsorption heats vs coverage profiles of the four supported Pd−Ce catalysts and the corresponding nonpromoted supported Pd samples reduced at 773 K are compared in Figure 10a−d. The addition of Ce reduces the initial adsorption heat by ca. 25 kJ/mol on all the samples. This means that the presence of Ce weakens the adsorption strength of CO on Pd. This fact may be explained in different ways: (i) the CeO_2 occupies the highly coordinated surface palladium sites, e.g., 3-fold hollow sites on Pd (111), which are the strongest sites for CO adsorption; (ii) a Pd−CeO_2 interaction may occur[32] leading to electron transfer from Pd to CeO_2; (iii) the CO is adsorbed in a tilted mode due to the interaction with partially reduced CeO_2, and thus decreases the strength of the Pd−C bond. The IR spectra (Figure 9) show that the Ce addition enhances the population of Pd (111) planes at the surface palladium particles, these Pd (111) planes being predominant on the Pd (100) ones. This fact is manifested by the relative intensity of the bands at ca. 1980 and 1920 cm^{-1}, which stem from bridged CO on Pd (100) and Pd (111) planes, respectively.[25]

3.4. Pd Dispersion Based on CO Chemisorption. Table 1 lists the initial adsorption heats, CO adsorption amounts, and Pd dispersions of different supported Pd samples. The Pd dispersions of various catalysts were calculated by assuming a Pd/CO = 1 stoichiometry. From the data of Table 1, it can be inferred that an increase of the reduction temperature produces a decrease in the amount of CO adsorbed; i.e., Pd dispersion decreases, especially for ZrO_2 and ZrO_2−La_2O_3 supported samples. In the presence of Ce, the initial adsorption heat decreases and the amount of CO adsorbed increases; i.e., Pd dispersion increases, especially for ZrO_2 and ZrO_2−La_2O_3 supported samples.

However, the analysis of the microcalorimetry and IR results invalidates the simple relation between CO adsorbed amount and palladium dispersion exposed above. Thus, the values of Pd dispersion in Table 1, which were calculated assuming that one surface palladium atom adsorbs one CO molecule, do not give real surface information for the following two reasons. First, there are several kinds of CO adsorption states, including linear, bridged, and multibonded. When CO is at bridged or multibonded states, one adsorbed CO molecule corresponds to two, three, or more Pd atoms. Usually bridged CO is predominant on the Pd catalysts. Second, the fraction of each CO adsorption state varied with supports. For instance, there are more adsorbed CO at linear state on Pd/ZrO_2 than on Pd/Al_2O_3, and obviously, the Pd dispersion will not be accurate if the same Pd/CO value is used to calculate Pd dispersion for the two catalysts. Therefore, the Pd dispersions listed in Table 1 are only semiquantitative, and a correctness factor, based on the percentages of various CO adsorption states, must be introduced to get accurate Pd dispersion values.

4. Conclusions

In summary, a good correlation between the results of microcalorimetry and IR for CO adsorption on palladium catalysts was found, and the following points can be concluded:

1. The CO is adsorbed on palladium catalysts in three different modes: multibonded (3-fold), bridged (2-fold, both on Pd (111) and (100) planes), and linear (1-fold) with differential heats of adsorption liying on the high (210−170 kJ/mol), medium (160−120 kJ/mol), and low (110−70 kJ/mol) field, respectively.

2. The support material, the reduction temperature, and the treatment conditions affect the surface morphology of the Pd catalysts, and as a result, the fraction of sites

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adsorbing the CO in a specific mode is influenced. The presence of Ce weakens the adsorption strength of CO on palladium.

3. Pd (111) planes are predominant on the catalysts in reduced state, although the Pd (100) planes are enhanced after methane combustion reaction. Upon CO adsorption, the 3-fold sites on the Pd (111) surface are first occupied at low CO coverage, but at high and/or saturation coverage the CO molecules became bridged and linearly bonded.

4. A correctness factor must be introduced when one calculates the Pd dispersion using the total CO adsorption amount, because most of the adsorbed CO molecules are in bridged state and the proportion of sites is affected by the support.

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