Effects of Reduction Temperature and Metal–Support Interactions on the Catalytic Activity of Pt/γ -Al₂O₃ and Pt/TiO_2 for the Oxidation of CO in the Presence and Absence of H₂

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TiO₂- and γ -Al₂O₃-supported Pt catalysts were characterized by HRTEM, XPS, EXAFS, and *in situ* FTIR spectroscopy after activation at various conditions, and their catalytic properties were examined for the oxidation of CO in the absence and presence of H₂ (PROX). When γ -Al₂O₃ was used as the support, the catalytic, electronic, and structural properties of the Pt particles formed were not affected substantially by the pretreatment conditions. In contrast, the surface properties and catalytic activity of Pt/TiO₂ were strongly influenced by the pretreatment conditions. In this case, an increase in the reduction temperature led to higher electron density on Pt, altering its chemisorptive properties, weakening the Pt–CO bonds, and increasing its activity for the oxidation of CO. The *in situ* FTIR data suggest that both the terminal and bridging CO species adsorbed on fully reduced Pt are active for this reaction. The high activity of Pt/TiO₂ for the oxidation of CO can also be attributed to the ability of TiO₂ to provide or stabilize highly reactive oxygen species at the metal–support interface. However, such species appear to be more reactive toward H₂ than CO. Consequently, Pt/TiO₂ shows substantially lower selectivities toward CO oxidation under PROX conditions than Pt/ γ -Al₂O₃.

Introduction

Supported Pt catalysts are employed in several large-scale industrial applications including among others oxidation, hydrogenation, and hydrocarbon rearrangement reactions.¹ The properties of Pt in these catalysts are determined not only by the metal surface structure and dispersion, but also by the metal-support interaction. For example, more than two decades ago it was demonstrated that platinum-group metals supported on TiO₂ exhibit a strong dependence of their CO and H₂ chemisorptive properties on the reduction protocol used to treat these catalysts.² This phenomenon, described by the term Strong Metal-Support Interaction (SMSI), has been the subject of extensive investigation.³ The results reported in the literature indicate that the SMSI effect also influences the catalytic performance of supported metals in hydrogenation and hydrogenolysis reactions.³ Several explanations suggested for the interpretation of SMSI were based on electronic and structural effects involving both the active metal and fragments of the support.^{3,4} Results of more recent work focusing on clusterderived catalysts suggest that reactants, as well as fragments of the support, may be viewed as ligands capable of affecting the structure and, therefore, the catalytic properties of supported metals.^{5–7} This effect is maximized for small supported metal clusters incorporating only a few metal atoms, which have properties distinctly different from those of bulk metals.⁸ As the size of these clusters grows, the fraction of the metal atoms located at the metal-support interface progressively decreases, hence the effect of the support becomes negligible for very large

particles. However, the question of how big metal particles should be for their catalytic properties to become independent of the nature of the support remains open. Furthermore, limited attention has been paid to the influence of metal-support interactions on reactions taking place in oxidative environments.

The goal of the work summarized in this paper was to determine how the nature of the metal-support interactions could affect the dispersion, electronic, chemisorptive, and catalytic properties of Pt in reactions in which O₂ participates as a reactant. More specifically, our interest is focused on the oxidation of CO in the presence and absence of H2 over TiO2and y-Al₂O₃-supported Pt catalysts. These reactions have attracted substantial attention in recent years due to their potential application in hydrogen purification schemes for fuel cell use, as well as indoor/cabin air cleanup.^{9,10} The TiO₂- and γ -Al₂O₃-supported platinum catalysts were characterized in detail by HRTEM, XPS, EXAFS, and FTIR spectroscopy. Results from these efforts were combined with catalytic data to determine how various factors influence the activity of the supported Pt particles in the oxidation of CO in air, as well as in H₂-rich mixtures.

Experimental Methods

Reagents and Materials. The γ -Al₂O₃ support with a BET surface area of 100 m²/g was prepared by forming a paste of aluminum oxide C (Degussa) in dionized water, followed by drying at 120 °C and calcination at 500 °C in air for 24 h. The TiO₂ powder (Kemira) with a BET surface area of 72 m²/g was also calcined in air at 500 °C for 12 h prior to use. H₂, N₂, and He (all UHP grade; National Welders) were purified prior to their use by passage through oxygen/moisture traps (Model OT3-2, Agilent) capable of removing traces of O₂ and water to

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15 and 25 ppb, respectively. O₂ and CO (National Welders) were purified prior to their use by passage through a moisture trap (Model GMT-2GCHP, Agilent) capable of removing water to 25 ppb. The $H_2PtCl_6•6H_2O$ precursor (99.95% purity, Alfa Aesar) was used as supplied.

Catalyst Preparation. Pt/TiO₂ and Pt/ γ -Al₂O₃ were prepared by incipient wetness impregnation of the corresponding supports with an aqueous solution of H₂PtCl₆•6H₂O, followed by drying in air at 110 °C for 24 h. The amounts of the precursor were chosen to yield samples containing 1 wt % of Pt. Prior to further characterization, each sample was treated with H₂ as described below.

FTIR Spectroscopy. FTIR spectra were collected with a Nicolet Nexus 470 spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. Powder samples were pressed into self-supported wafers and mounted in the IR cell, which was connected to a gas distribution manifold. The design of the IR cell has been described elsewhere.¹¹ Samples were pretreated in H₂ flow at the 200–400 °C temperature range for 2 h prior to each measurement. After the reduction treatment was completed, the cell was flushed with He for 15 min and cooled to room temperature in flowing He. Spectra were recorded at a spectral resolution of 2 cm⁻¹ accumulating 64 scans per spectrum.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were collected with an X-ray High-Resolution Photoelectron Spectrometer (Quantum 2000, Physical Electronics), using a focused monochromatic Al K α beam with an energy of 1486.7 eV, that was rastered over 0.28 mm² of the sample area. The spectrometer was equipped with a Spherical Capacitor Energy Analyzer incorporating a 16-element multichannel detector. Prior to these measurements, each sample was treated with H₂ at 200-400 °C or O₂ at 300 °C in a glass reactor connected to a gas distribution system. After the treatment was completed, the reactor was sealed and transferred into a glovebox, where the sample was loaded on the standard sample holder that was transferred to the analysis chamber without air exposure. The residual gas pressure in the analysis chamber was 5×10^{-8} Torr. The Ti (2p) line (458.7 eV) was used to calibrate the binding energies that were measured with an accuracy of ± 0.2 eV. Low-energy electrons and argon ions were used for specimen neutralization.

Transmission Electron Microscopy (TEM). TEM images were obtained with a 200 keV high-resolution transmission electron microscope (JEOL 2010F) having a specific point-topoint resolution of 0.194 nm. All images were digitally recorded with a multiscan charge-coupled device camera (Model 794, Gatan) with 1024×1024 pixel resolution and further analyzed with a digital micrograph (Gatan). During a typical sample preparation for TEM imaging, approximately 15 mg of sample was finely dispersed and embedded in a L. R. White resin. Then, the sample was sectioned by using a RMC MT 6000 microtome to slices with a thickness of approximately 50 nm and deposited onto a Cu grid. Average particle sizes were determined by measuring at least 200 particles from 20 different micrographs. The statistical analysis used to determine the surface-mean particle sizes was similar to that reported elsewhere.¹² The accuracy of determining the mean size was estimated to be on the order of $\pm 15\%$.

Catalytic Measurements. Steady-state catalytic activity measurements for the preferential oxidation of CO under excess H_2 (PROX) were performed in a quartz single-pass fixed-bed microreactor at atmospheric pressure. The temperature inside the reactor was monitored by a thermocouple extending into

the catalyst bed. Samples in a powder form (0.077 g) were diluted 90 times by weight with quartz particles (60-80 mesh)to keep the catalyst bed isothermal. The total volumetric flow rate of the reactant mixture was held at 154 mL/min (1atm, 25 °C) yielding a corresponding Gas Hourly Space Velocity (GHSV) of 120 000 mL/g·h. Reacting gases were mixed in a gas distribution system, while the flow of each gas was controlled by a mass flow controller (Model 201-DKASVBAA, Porter) to create an accurate and reproducible feed containing 0.5% of CO, 0.5% of O₂, 45% of H₂, and 54% of N₂. Before mixing, the CO/N₂ mixture was heated to 350 °C in a quartz trap to eliminate any carbonyls that may have been formed in the storage cylinder. The feed and the reaction products were analyzed with on-line single beam NDIR CO (Ultramat 23, Siemens) and O₂ (Model 201, AMI) analyzers capable of detecting CO and O_2 in the 0-250 and 0-1000 ppm ranges, respectively. The outputs from both analyzers and the temperature controller were linked to a user interface with Labview software. The reaction selectivity toward the formation of CO₂ was calculated as the amount of O2 consumed in the CO oxidation reaction (calculated from the CO balance) over the total amount of O₂ consumed.

The catalytic oxidation of CO in the absence of H₂ was carried out in equipment similar to that described above, at atmospheric pressure, a GHSV of 120 000 mL/g·h, and temperatures between 30 and 300 °C. The reaction feed contained 1% of CO balanced with air. Both the reaction feed and products were analyzed with an on-line single-beam NDIR (Ultramat 23, Siemens) analyzer capable of detecting CO in the 0–500 ppm and 0–5% ranges and CO₂ in the 0–5% range.

Prior to any catalytic measurements, the samples were treated with H₂ or O₂, while the temperature was ramped at 5 °C/min and held at the desired temperature for 2 h. In the absence of a catalyst, there was no measurable conversion of CO for either reaction in the temperature range of interest (i.e., up to 300 °C).

EXAFS Spectroscopy. EXAFS data were collected at X-ray beamline X-18B of the National Synchrotron Light Source (NSLS), Brookhaven National laboratory, Upton, NY. The storage ring energy was 2.8 GeV and the ring current 110–270 mA.

The Pt/ γ -Al₂O₃ samples were loaded in a wafer form into an *in situ* EXAFS cell¹³ connected to a gas distribution system, allowing for the *in situ* treatment of samples in various atmospheres. After the desired treatment was completed, the EXAFS cell was evacuated to 10^{-5} Torr at room temperature, cooled to liquid nitrogen temperature, and aligned in the X-ray beam. The EXAFS data were recorded in the transmission mode with an appropriate amount of sample to give an absorbance of approximately 2.5 at the Pt L₃ (11563.7 eV) edge.

Data for Pt/TiO_2 samples were recorded in the fluorescence mode with a 13th element Ge detector. Samples in powder form were reduced in H₂ at the desired temperature, purged with He at the same temperature, cooled to room temperature in He flow, and mounted on the sample holder while exposed to air. Data were collected at room temperature with a Si(111) double-crystal monochromator that was detuned by 20% to minimize the effects of higher harmonics in the X-ray beam.

The EXAFS data were analyzed with experimentally determined reference files obtained from EXAFS data characterizing materials of known structure, as stated elsewhere.¹⁴ The EXAFS parameters were extracted from the raw data with the aid of the XDAP software.¹⁵ The methods used to extract the EXAFS function from raw data are essentially the same as those reported elsewhere.¹⁶ The data used for each sample were the average

TABLE 1: Average Size of Pt Particles in Pt/γ -Al₂O₃ and Pt/TiO_2 Following Reduction at Different Temperatures

	reduction	Average Pt diameter (Å)				
sample	temp (°C)	HRTEM	EXAFS			
1.0% Pt/y-Al ₂ O ₃	200		9			
	300		11			
	400		11			
1.0% Pt/TiO ₂	200	25	25			
	400	14	26			

of five scans. The data at the Pt L₃ edge were analyzed with a maximum of 16 free parameters over the ranges of $3.50 < k < 15.50 \text{ Å}^{-1}$ (*k* is the wave vector) and 0.0 < r < 5.0 Å (*r* is the distance from the absorbing atom; in this case Pt). The statistically justified number of free parameters, *n*, was found to be 39, as estimated on the basis of the Nyquist theorem:^{17,18} $n = (2\Delta k\Delta r/\pi) + 1$, where Δk and Δr , respectively, are the *k* and *r* ranges used in the data fitting. The parameters characterizing both the high-*Z* (Pt-Pt) and low-*Z* (Pt-O_{support}) contributions were determined by multiple-shell fitting in *R*-space with application of k^1 and k^3 weighting in the Fourier transformations.¹⁶ The fit was optimized by use of a difference file technique with phase- and amplitude-corrected Fourier transforms forms of the data.^{19,20}

Results

Platinum Dispersion. The average Pt particle sizes in the Pt/γ -Al₂O₃ and Pt/TiO_2 systems after various pretreatments were estimated from EXAFS data based on known relationships between the average size of metal particles and the metal—metal first-shell coordination number.^{21,22} The results obtained (Table 1) indicate that when γ -Al₂O₃ was used as the support, small platinum particles with an average diameter of approximately 9 Å were formed after reduction at 200 °C. An increase of the reduction temperature up to 400 °C had no substantial effect on the Pt particle size and dispersion (i.e., the fraction of metal atoms exposed at the surface) with the average Pt particle size remaining at approximately 11 Å. Assuming a spherical shape for these metal particles, the Pt dispersion in these samples was found to be almost 100%.

Following the hydrogen treatment at 200 °C Pt particles with an average diameter of approximately 25 Å were formed in the case of Pt/TiO₂ as indicated by both the HRTEM and EXAFS data (Table 1). The HRTEM data (Table 1, Figure 1) further indicate that an increase of the reduction temperature to 400 °C was accompanied by a decrease of the average Pt size from 25 Å to approximately 14 Å. However, the EXAFS data suggest that the size of Pt particles remained unchanged (Table 1). This discrepancy between the results obtained from the two different techniques can be rationalized in terms of SMSI behavior, as discussed in detail later.

XPS Measurements. The binding energies of the Pt (4f) core level region and the Pt/Ti atomic ratios for Pt/TiO₂ samples treated with O₂ or H₂ at various temperatures are reported in Table 2. The corresponding XPS spectra of the Pt (4f) region are shown in Figure 2. When the Pt/TiO₂ sample was treated with O₂ at 300 °C, the XPS spectrum was characterized by two peaks corresponding to the Pt (4f_{5/2}) and Pt (4f_{7/2}) photoemission lines centered at 75.4 and 72.1 eV, respectively. Following exposure of the same sample to H₂ at 200 °C both peaks shifted to lower binding energies by approximately 0.4 eV. Subsequent treatment with H₂ at 400 °C resulted to an additional shift of the Pt (4f) lines to even lower binding energies of 74.6 and 71.3 eV for the Pt (4f_{5/2}) and Pt (4f_{7/2}) peaks, respectively (Figure 2). No differences were observed in the relative amounts of the



Figure 1. Particle size distributions as estimated by TEM for 1 wt % Pt/TiO_2 samples reduced with H_2 at 200 and 400 °C.



Figure 2. XPS spectra of the Pt(4f) core level region for 1 wt % Pt/ TiO₂ samples treated with O_2 or H_2 at various temperatures.

TABLE 2: Summary of XPS Data Obtained for Pt/TiO₂

treatment gas/ temp (°C)	Pt 4f _{5/2} (eV)	Pt 4f _{7/2} (eV)	Pt/Ti
O ₂ /300	75.4	72.1	0.012
$H_2/200$	75.0	71.7	0.011
$H_2/400$	74.6	71.3	0.009

surface Pt (i.e., Pt/Ti atomic ratio) between samples treated in O_2 at 300 °C and in H_2 at 200 °C. However, the Pt/Ti atomic ratio decreased beyond the margin of error as the reduction temperature was increased to 400 °C (Table 2).

Infrared Spectra of CO Adsorbed on Pt/ γ -Al₂O₃. When Pt/ γ -Al₂O₃ was reduced in H₂ at 200 °C and exposed to 75 Torr of CO at room temperature, three bands were observed in the $\nu_{\rm CO}$ region at 2110 (vw), 2062 (s), and approximately 1820 (w) cm⁻¹ (Figure 3A). These bands can be assigned to linear CO on Pt²⁺ and Pt⁰ sites, and bridging CO on Pt⁰ sites, respectively.²³ The intensity of the peak associated with CO coordinated on Pt²⁺ sites was small and its contribution to the



Figure 3. FTIR spectra of CO adsorbed at room temperature on (A) 1 wt % Pt/γ -Al₂O₃ and (B) 1 wt % Pt/TiO_2 reduced in H₂ at different temperatures.

total absorption was less than 1%, consistent with the notion that almost all Pt was effectively reduced at this temperature to the metallic state. Furthermore, the band at 2110 cm⁻¹ was not detectable in the infrared spectra obtained with samples reduced at higher temperatures, indicating reduction of Pt to an even higher extent under these conditions. The only difference observed in this case was a decrease in the intensity of the two bands associated with Pt⁰ for the sample reduced at 400 °C, indicating that some sintering of the Pt particles has taken place during this pretreatment.

FTIR data further show that the CO species are relatively weakly adsorbed on Pt/γ -Al₂O₃ and can be removed by heating of the sample in He flow. The desorption of CO did not depend on the reduction temperature and typically proceeded as shown in Figure 4A. The bridging CO band at 1820 cm⁻¹ disappeared first at approximately 285 °C, while the linear CO band at 2062 cm⁻¹ declined in intensity, broadened, shifted to 2030 cm⁻¹, and finally disappeared at approximately 400 °C (Figure 4A). These results are also summarized in Table 3.

Infrared Spectra of CO Adsorbed on Pt/TiO₂. Similar to the results obtained with Pt/γ -Al₂O₃, when Pt/TiO₂ was reduced in H₂ at 100 °C and exposed to 75 Torr of CO at room temperature, bands of terminal and bridging CO species



Figure 4. FTIR spectra collected during the desorption of CO from (A) 1 wt % Pt/γ -Al₂O₃ reduced at 400 °C and (B) 1 wt % Pt/TiO_2 reduced at 200 °C, following treatment in He at various temperatures.

TABLE 3: Thermal Stability of Adsorbed CO Species

sample	reduction temp (°C)	temp of complete CO desorption (°C)
1.0% Pt/γ-Al ₂ O ₃	200	400
	300	400
	400	400
1.0% Pt/TiO ₂	200	60
	300	25
	400	25

adsorbed on fully reduced Pt sites were observed at 2076 (s) and 1830 (w) cm⁻¹, respectively (Figure 3B). An increase of the reduction temperature to 200 °C had no substantial effect on either the intensity or frequency of these bands. However, when the reduction temperature was further increased to 300 °C, the band at 2076 cm⁻¹ declined dramatically in intensity and appeared as a shoulder to a new band observed at 2060 cm⁻¹ (Figure 3B, spectrum 3). The presence of bridging CO species remained evident in the spectrum, although the intensity of the corresponding band was very low. The intensities of all these bands further declined as the reduction temperature was increased to 500 °C, although the characteristic frequencies of these bands remained unchanged (Figure 3B, spectra 3–5).

The FTIR data further indicate that the various CO species adsorbed on Pt/TiO_2 can be removed by thermal treatment in He (Figure 4B). However, the pattern observed during the

desorption of CO in this case appeared to be different from that observed for the Pt/γ -Al₂O₃ samples. For example, the adsorption of CO on the Pt/TiO_2 sample reduced at 200 °C was much weaker and complete desorption of CO was achieved at much lower temperatures. The bridging species were no longer detectable as the temperature was increased to 38 °C, while the terminal CO species completely disappeared at temperatures as low as 60 °C (Figure 4B). Moreover, as the intensity of the linear CO band at 2076 cm⁻¹ decreased with desorption temperature, no apparent shift of the band position was observed (Figure 4B). Similar behavior was also observed with the samples reduced at higher temperatures, although complete desorption of CO was observed in these cases even at room temperature (Table 3).

Kinetic and in Situ FTIR Monitoring of the Oxidation of CO by Air. The CO conversions observed at various temperatures over 1 wt % Pt/y-Al₂O₃ samples pretreated under different conditions are shown in Figures 5A and 5B. Almost identical results were obtained for the samples reduced in H₂ at 300 or 400 °C with 100% conversion being reached in each case at 240 °C. Reduction at lower temperature (200 °C) did not influence the light-off curve in the 50-200 °C temperature range. However, after attaining approximately 60% CO conversion at 216 °C, the reaction rate was decreased in the 216-235 °C temperature range, and then again increased with 100% CO conversion eventually reached at 260 °C. When an oxidation pretreatment at 300 °C was used instead of reduction, the lightoff curve characteristics were almost identical with those observed with the sample reduced at 200 °C (Figure 5B). However, a subsequent treatment in H₂ at 400 °C resulted in a sample indistinguishable from the one originally pretreated in H₂ at 400 °C (Figures 5A and 5B).

Similar light-off curves obtained with 1 wt % Pt/TiO₂ samples pretreated under different conditions are shown in Figure 6. The light-off curves in this case are shifted toward lower temperatures, indicating the higher activity of the Pt/TiO₂ samples for the oxidation of CO. Furthermore, the performance of these samples was substantially affected by the pretreatment protocol. More specifically, while complete CO conversion was reached at 210 °C for the sample pretreated in O₂ at 300 °C, over the samples reduced in H₂ at 200 °C or 300 °C complete CO conversion was observed at 200 and 178 °C, respectively. Further increase of the reduction temperature to 400 °C did not result in any further shift of the light-off temperature, although this sample exhibited noticeably higher CO conversions in the 50-150 °C temperature range than samples reduced at lower temperatures (Figure 6).

Figure 7 provides a direct comparison of the CO oxidation over Pt/TiO₂ and Pt/ γ -Al₂O₃ samples pretreated in H₂ at 400 °C. The results demonstrate the higher activity of the Pt/TiO₂ sample. The pure TiO₂ and γ -Al₂O₃ supports also exhibited limited activity at temperatures above 300 °C.

In situ FTIR experiments were conducted in parallel to the kinetic measurements under similar experimental conditions with the infrared cell serving as a flow reactor. Spectra of Pt/TiO₂ and Pt/ γ -Al₂O₃ samples exposed to the reaction mixture (1% CO/air) at different temperatures are shown in Figure 8, parts A and B, respectively. Exposure of Pt/ γ -Al₂O₃ to the reaction mixture at 25 °C led to the appearance of three bands at 2121 (wv), 2067 (s), and 1832 (w) cm⁻¹ (Figure 8B), which are similar to those observed during the adsorption of CO in the absence of O₂ (Figure 4A). The spectrum remained essentially unchanged at temperatures up to 115 °C. As the reaction temperature was increased further, the bands at 1832 and 2067



Figure 5. CO conversions versus temperature observed during the oxidation of CO in air over 1 wt % Pt/γ -Al₂O₃ samples pretreated (A) in H₂ at (\blacktriangle) 200, ($\textcircled{\bullet}$) 300, and (\blacksquare) 400 °C and (B) in (\bigstar) H₂ at 200 °C, ($\textcircled{\bullet}$) O₂ at 300 °C, and (\blacksquare) O₂ at 300 °C followed by H₂ at 400 °C.

cm⁻¹ declined in intensity and finally disappeared at approximately 200 °C, with the former being removed first. In contrast, the low-intensity band, initially observed in the spectrum at 2121 cm⁻¹, increased substantially in intensity as the temperature was raised to 170 °C, and remained present at temperatures as high as 300 °C (Figure 8B).

Similarly, when Pt/TiO₂ was exposed to the reaction mixture at room temperature, three carbonyl bands were observed at 2125 (wv), 2080 (s), and 1835 (w) cm⁻¹ (Figure 8A, spectrum 1). These bands remained unchanged as the reaction temperature was increased to 105 °C. A substantial change was observed beyond this point, with the band at 1835 cm⁻¹ disappearing from the spectrum and the band at 2080 cm⁻¹ significantly declining in intensity, and eventually disappearing as the reaction temperature reached 140 °C (Figure 8A, spectrum 6). The band at 2125 cm⁻¹ also declined in intensity with increasing reaction temperature, but remained visible in the spectrum even at 160 °C (Figure 8A, spectrum 7).

Curves characterizing the removal of CO species from the surface of Pt/TiO_2 as a function of the reaction temperature are compared in Figure 9. These data were extracted from *in situ* FTIR spectra and show that when the sample was reduced at



Figure 6. Light-off curves characterizing the oxidation of CO in air over 1 wt % Pt/TiO₂ samples pretreated in (\bullet) O₂ at 300 °C, or H₂ at (\bullet) 200, (\blacktriangle) 300, and (\blacksquare) 400 °C. (GHSV= 120 000 mL/g·h; 1% CO balanced with air).



Figure 7. Light-off curves demonstrating the effect of the support on the oxidation of CO in air over (**I**) 1% Pt/TiO₂, (**A**) 1% Pt/ γ -Al₂O₃ pretreated with H₂ at 400 °C, (**\diamond**) pure TiO₂ treated in H₂ at 300 °C, and (**\nabla**) pure γ -Al₂O₃ treated in H₂ at 300 °C.

300 °C or higher temperatures, almost all CO species were removed from the Pt surface at 80 °C. However, when the sample was reduced at 200 °C or, alternatively, oxidized at 300 °C, temperatures of about 140 and 225 °C, respectively, were required. Similar information extracted from FTIR spectra of the Pt/ γ -Al₂O₃ (not shown) indicate no substantial differences between samples reduced at various temperatures.

Selective Oxidation of CO in H₂-Rich Mixtures. The conversions of CO and O₂ at different temperatures during the selective oxidation of CO in the presence of excess H₂ over the 1 wt % Pt/ γ -Al₂O₃ sample reduced in H₂ at 300 °C are shown in Figure 10. In both cases the conversions increased in parallel, to almost 100% as the temperature was increased to 210 °C. During this process the selectivity remained in the neighborhood of 50%. Further increase of the reaction temperature to 233 °C was accompanied by a decrease in the CO conversion to 85% and the CO selectivity to 42%, while the O₂ conversion



Figure 8. In situ FTIR spectra collected at various reaction temperatures in 1% CO in air over (A) a 1 wt % Pt/TiO₂ sample prereduced at 200 °C and (B) a 1 wt % Pt/ γ -Al₂O₃ sample prereduced at 300 °C.

remained at 100%. No differences were observed with samples reduced at temperatures between 200 and 400 $^{\circ}$ C.

Similar light-off curves obtained over bare TiO_2 and a 1 wt % Pt/TiO_2 sample are shown in Figure 11. Over the TiO_2 support pretreated in H₂ at 300 °C the CO conversion became measurable only at temperatures above 200 °C (Figure 11). The consumption of O₂ was slightly higher than that of CO at every reaction temperature examined, reflecting the relatively low selectivity for CO oxidation, which was in the range 16–32%.

The 1 wt % Pt/TiO₂ sample pretreated in H₂ at 200 °C exhibited much higher activity than that of the bare TiO₂ support with a maximum CO conversion of approximately 62% observed at 252 °C. Substantial consumption of O₂ was observed with this sample at reaction temperatures as low as 70 °C, and complete O₂ conversion was reached at 140 °C (Figure 11).

Some significant changes were observed in the light-off characteristics of both CO and O_2 when the 1 wt % Pt/TiO₂ sample was pretreated in H₂ at 300 °C. Approximately 10% of the O_2 in this case was already consumed at 30 °C, while complete O_2 conversion was observed at 115 °C. In contrast, the CO light-off curve exhibited two maxima, one of approximately 30% at 70 °C, and one (similar to what was observed with the sample pretreated at 200 °C) of approximately



Figure 9. Curves characterizing the removal of CO from the Pt surface during CO oxidation by air over 1 wt % Pt/TiO₂ treated with (\odot) O₂ at 300 °C, (\blacksquare) H₂ at 200 °C, and (\blacktriangle) H₂ at 300 °C. The surface concentration of CO species was determined from *in situ* IR data recorded at various reaction temperatures and GHSV of approximately 75 000 mL/g·h.



Figure 10. Dependence of (\blacktriangle) CO and (O) O₂ conversion on the reaction temperature during the selective oxidation of CO in a H₂-rich stream over 1% Pt/ γ -Al₂O₃ reduced with H₂ at 300 °C.

60% at 250 °C. Almost identical behavior was also observed with the sample pretreated in H_2 at 400 °C.

Structural Characterization by EXAFS. The structural parameters characterizing the Pt species formed in the Pt/ γ -Al₂O₃ and Pt/TiO₂ samples after various treatments are summarized in Tables 4 and 5. The error bounds in these parameters represent precisions determined from statistical analysis of the EXAFS data with the XDAP software,¹⁵ and not accuracies. The estimated accuracies in the determination of the EXAFS parameters of the main contributions are as follows: coordination number (*N*), ±20%; distance (*R*), ±1%; Debye–Waller factor ($\Delta \sigma^2$), ±30%; inner potential correction (ΔE_0), ±10%.

Discussion

Platinum Dispersion. The dispersion of Pt in supported catalysts can be reliably determined from a variety of different techniques including the chemisorption of probe molecules (e.g.,



Figure 11. Dependence of $(\blacksquare, \blacktriangle, \bigtriangledown)$ CO and $(\bullet, \diamondsuit, \bigcirc)$ O₂ conversion on the reaction temperature during the selective oxidation of CO in a H₂-rich stream over TiO₂ ($\bigtriangledown, \bigcirc$) treated with H₂ at 300 °C and over 1% Pt/TiO₂ reduced with H₂ at (\bullet, \blacktriangle) 200 °C and ($\blacksquare, \blacklozenge$) 300 °C.

H₂, O₂, or CO), HRTEM, and EXAFS.^{21,24} The data of Table 1 indicate that when an aqueous solution of H2PtCl6•6H2O was used as the precursor for the preparation of Pt/γ -Al₂O₃, the subsequent drying and reduction with H₂ at 200 °C led to the formation of small Pt particles with an average diameter of 9 Å. Similarly sized particles were obtained when an air exclusion technique was used to prepare Pt/y-Al₂O₃ from a [PtCl₂(PhCN)₂] precursor.⁶ When the reduction temperature was increased to 300 °C, the average diameter of the metal particles was also increased to approximately 11 Å, indicating that limited agglomeration of Pt took place after such a treatment. Further increase of the reduction temperature to 400 °C appeared to have no additional effect on the Pt dispersion (Table 1), indicating the relatively high thermal stability of Pt on the γ -Al₂O₃ surface under these conditions. These results are in good agreement with earlier reports illustrating the high resistance of y-Al₂O₃-supported Pt to sintering even after oxidationreduction treatments at 200-400 °C.21

Larger Pt particles were obtained with the Pt/TiO₂ system. The HRTEM data indicate that the average Pt particle size in this case was approximately 26 Å after reduction at 200 °C (Table 1). The EXAFS data (Table 4) indicate that this sample is characterized by a first-shell Pt-Pt coordination number of 9.1 at a distance of 2.75 Å, which in turn yields an average Pt particle size of approximately 25 Å,²² in good agreement with the HRTEM results. Substantial Pt-O contributions were also observed in this sample at 2.16 and 2.25 Å signifying interactions of Pt with the oxygen atoms of the support, as well as with oxygen atoms adsorbed on Pt due to its exposure to air during the data acquisition process in the fluorescence mode for this particular sample, although at this point we cannot distinguish between chemisorbed oxygen and oxygen associated with the support. Nevertheless, the presence of substantial Pt-Pt contributions in this sample is consistent with the presence of relatively large Pt particles the structure of which is not affected substantially by interactions with O2. In contrast, in the case of small metal clusters or particles, it is expected that the interaction with O₂ will lead to gradual oxidative fragmentation of the platinum clusters, ultimately leading to a complete loss of Pt-Pt bonds and to the formation of platinum oxide species.²⁵ It has been reported, for example, that exposure to

TABLE 4: Summary of the EXAFS Data Characterizing the Pt/TiO₂ Samples after Various Treatments^a

treatment gas/ temp (°C)	shell	Ν	R(Å)	$10^{3}\Lambda\sigma^{2}$ (Å ²)	ΔE_0 (eV)
			()		
$H_2/200$	Pt-Pt	9.1 ± 0.4	2.75 ± 0.01	5.4 ± 0.4	-0.1 ± 0.3
	Pt-O _{support}				
	Pt-O1	3.1 ± 0.9	2.16 ± 0.02	5.9 ± 0.8	-13.2 ± 0.5
	Pt-O2	5.3 ± 0.3	2.25 ± 0.02	10.0 ± 1.1	9.3 ± 0.8
H ₂ /400	Pt-Pt	9.3 ± 0.5	2.76 ± 0.01	4.7 ± 0.4	-0.3 ± 0.3
	Pt-O _{support}				
	Pt-O1	3.4 ± 0.1	2.18 ± 0.02	6.8 ± 0.1	-17.2 ± 0.4
	Pt-O2	5.9 ± 0.3	2.28 ± 0.02	10.0 ± 1.2	3.8 ± 0.6
	11 01	010 ± 010		1010 ± 115	010 ± 010

^{*a*} Notation: *N*, coordination number; *R*, distance between absorber and backscatterer atoms; $\Delta \sigma^2$, Debye–Waller factor; ΔE_0 , inner potential correction.

TABLE 5:	Summary	of the	EXAFS	Data	Characterizing	the	Pt/	γ-Al ₂ O ₃	Samp	les afte	er Various	Treatments ^{<i>a</i>}
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		-			
treatment gas/temp (°C)	shell	Ν	R (Å)	$10^{3}\Delta\sigma^{2}$ (Å ²)	$\Delta E_0 ({ m eV})$
H ₂ /400	Pt-Pt first	6.1 ± 0.1	2.72 ± 0.01	5.8 ± 0.1	0.7 ± 0.2
	Pt-Pt second	2.2 ± 0.1	3.91 ± 0.01	9.0 ± 0.3	-8.0 ± 0.3
	Pt-O _{support}				
	$Pt-O_s$	0.7 ± 0.1	2.12 ± 0.01	10.0 ± 1.0	-1.6 ± 0.2
	Pt-O ₁	0.8 ± 0.1	2.74 ± 0.01	1.0 ± 0.6	-2.2 ± 0.5
H ₂ /300	Pt-Pt first	6.0 ± 0.1	2.72 ± 0.01	5.5 ± 0.1	-1.3 ± 0.1
	Pt-Pt second	2.1 ± 0.1	3.88 ± 0.02	10.0 ± 1.0	-2.6 ± 0.5
	Pt-O _{support}				
	Pt-O _s	0.6 ± 0.1	2.10 ± 0.01	10.0 ± 1.3	0.7 ± 0.3
	Pt-O ₁	1.1 ± 0.1	2.70 ± 0.01	3.8 ± 0.5	2.1 ± 0.4
H ₂ /200	Pt-Pt first	4.5 ± 0.1	2.72 ± 0.01	4.0 ± 0.1	-3.9 ± 0.1
	Pt-Pt second	2.2 ± 0.1	3.91 ± 0.01	9.0 ± 0.3	-8.0 ± 0.3
	Pt-O _{support}				
	Pt-O _s	0.9 ± 0.1	2.13 ± 0.01	10.0 ± 1.1	-2.0 ± 0.3
	Pt-O ₁	1.1 ± 0.1	2.65 ± 0.01	0.2 ± 0.3	4.5 ± 0.4
$H_2/200$ then CO + air/160	Pt-Pt	4.1 ± 0.1	2.79 ± 0.01	7.7 ± 0.2	-4.6 ± 0.2
	Pt-O _{support}				
	Pt-O _s	2.0 ± 0.1	2.25 ± 0.02	-0.6 ± 0.1	-13.4 ± 0.4
	$Pt-O_1$	1.6 ± 0.2	2.64 ± 0.01	10.0 ± 1.0	-4.7 ± 0.4
$H_2/200$ then CO + air/280	Pt-Pt	3.1 ± 0.1	2.78 ± 0.01	0.8 ± 0.1	-1.0 ± 0.2
	Pt-O _{support}				
	Pt-O _s	2.8 ± 0.1	2.19 ± 0.01	1.0 ± 0.1	-8.5 ± 0.2
	Pt-O ₁	1.4 ± 0.1	2.68 ± 0.01	2.8 ± 0.7	-6.41 ± 0.4

^a Notation as in Table 4; the subscripts s and 1 refer to short and long, respectively.

 O_2 at room temperature was sufficient to break all the Pt–Pt bonds in γ -Al₂O₃-supported platinum clusters with an average diameter of about 10 Å.²⁶ This disintegration process was followed by EXAFS spectroscopy, where the formation of isolated platinum oxide clusters was confirmed.⁶

When the reduction temperature of Pt/TiO₂ was increased to 400 °C, the average diameter of the Pt particles estimated from HRTEM measurements was substantially different from that calculated based on the EXAFS data (Table 1). The HRTEM data indicate that the size of the Pt particles becomes smaller following reduction at 400 °C (Table 1, Figure 1). A redispersion of Pt has been previously observed in oxygen-rich atmospheres at elevated temperatures, and has been attributed to the oxidation of Pt particles to volatile species and the subsequent transport of such species over relatively large distances on the support surface.^{27–30} It also has been shown that the presence of chlorine during the oxidation can significantly enhance the Pt redispersion on γ -Al₂O₃ or TiO₂ due to the formation of [Pt^{IV}O_xCl_y] species from PtO₂.²⁸⁻³⁰ However, despite the presence of chloride ions in our case due to the use of the H2PtCl6•6H2O precursor, it is very unlikely that these species played an important role in the oxygen-free environment used. Moreover, in such a case a similar behavior would be expected from the Pt/γ -Al₂O₃ sample, which was not observed.

In contrast to the HRTEM data, the EXAFS results (Table 4) indicate that after reduction at 400 °C, the first-shell Pt-Pt coordination number and distance remain virtually unchanged,

consistent with the presence of metal particles having an average diameter of aproximately 26 Å. One possible explanation for this apparent discrepancy between HRTEM and EXAFS data in the case of Pt/TiO₂ sample is the unique nature of the interactions between Pt and the TiO₂ at elevated reduction temperatures, as suggested earlier for catalysts showing SMSItype behavior.³¹ The reduction of pure TiO₂ usually takes place at temperatures higher than 600 °C.²⁷ However, this process is accelerated in the presence of Pt. Temperature-programmed reduction (TPR) data, for example, indicate that the reduction of TiO₂ in this case begins at 300 °C, with a maximum observed at approximately 460 °C.27 It has been further suggested that H₂ atoms chemisorbed on Pt can interact with oxygen atoms from the support located at the metal-support interface to form oxygen vacancies and partially reduced Ti3+ sites.31 The subsequent strong interaction between exposed Ti3+ cations and Pt atoms located at the metal-support interface may then lead to the migration of partially reduced TiO_x support fragments onto the metal, resulting in a decrease of the exposed metal surface.³ If such decoration was to take place, it would result in underestimations of the metal particle sizes by HRTEM, consistent with our observations. At the same time, the EXAFS results should remain unchanged, since EXAFS probes the bulk of the Pt particles present. Such a decoration model is also consistent with the XPS and FTIR data discussed below. Nevertheless, additional detailed work-beyond the scope of the current paper-is needed to further probe the reasons for the observed discrepancy between HRTEM and EXAFS measurements and to reach definitive conclusions.

Electronic Structure of Platinum Particles. The photoemission doublet observed at 75.4 and 72.1 eV in the Pt (4f) region of the O₂-treated Pt/TiO₂ sample (Figure 2, Table 2) can be assigned to Pt²⁺ species present on the TiO₂ surface in the form of PtO. TPR data reported previously for a Pt/TiO₂ sample prepared from a similar precursor indicate the complete reduction of Pt at temperatures as low as 100 °C.²⁷ Consequently, the Pt 4f_{5/2} and Pt 4f_{7/2} peaks observed in the spectrum of the sample reduced with H₂ at 200 °C at 75.0 and 71.7 eV, respectively (Table 2, Figure 2), can be assigned to the fully reduced Pt species.

Further reduction at 400 °C results in a shift of the Pt (4f) lines to lower binding energies by approximately 0.4 eV. In addition to changes in the oxidation state and/or electron density, changes in metal dispersion may also result in shifts in the XPS spectra, since it has been shown that the Pt (4f) doublet is located at higher binding energies for smaller Pt particles.³² In contrast, a shift toward lower binding energies is observed when Pt particles become electron rich. It is possible that particle size and charge transfer effects may compensate each other to a certain degree. However, since Pt particle size remained virtually unchanged in the Pt/TiO₂ sample after reduction at 200-400 °C, as evidenced by the EXAFS data discussed in the previous section, the shift toward lower energies observed in the XPS spectra can be attributed to an increase in the electron density on Pt following reduction at elevated temperatures, consistent with an increased interaction between the Pt atoms and reduced fragments of the support. TiO₂ reduction in the presence of Pt has been confirmed previously by ESR measurements.³³ In fact, it was shown that after reduction at 300 °C the concentration of Ti³⁺ cations is 30 times higher in the presence of Pt than on the pure support. More recent XPS data show that formation of Ti³⁺ cations in the presence of Pt occurs at temperatures as low as 170 °C at the surface layers of TiO₂.³² Therefore, an electron transfer can be expected in this case from Ti³⁺ to Pt, if the Pt atoms and Ti^{3+} cations were to interact with each other. Such a transfer would enhance the electron density on Pt and result in a shift of the Pt (4f) doublet toward lower energies, consistent with our observations (Table 2).

It is worthy of note that the Pt/Ti atomic ratio, reflecting the relative amount of the surface Pt atoms, decreased as the reduction temperature was increased to 400 °C (Table 2). Similar results have been reported already for TiO2- and CeO2-supported Pt catalysts exhibiting the SMSI effects and were interpreted in terms of a screening effect for the emitted photoelectrons from Pt atoms.^{32,34} Such a screening could also be observed upon decreasing the amount of exposed Pt atoms due to sintering. More likely, however, the observed decrease of the Pt/Ti ratio as a function of the reduction temperature can be attributed to a decoration of Pt by TiO_x fragments of the support in agreement with earlier suggestions.^{3,4} It is interesting that our HRTEM and XPS data suggest that such a decoration of Pt can occur at temperatures as low as 400 °C, while typically this process is believed to take place at temperatures higher than 500 °C.35 Nevertheless, recent XPS, soft X-ray photoelectron spectroscopy, and low-energy ion scattering data confirm the possibility of Pt decoration by CeO_x and TiO_x suboxides in model catalysts at temperatures as low as 170 °C.32,34 Such decoration of Pt by a partially reduced TiO_x species would substantially increase the metal-support interface, and therefore, the number of possible contact points between Pt atoms and Ti³⁺ cations, resulting in the modification of electronic properties of Pt, consistent with our XPS data. Similar behavior was also observed in Rh/TiO₂, Rh/Ta₂O₅, Ni/Nb₂O₅, and Ni/TiO₂ samples. In these cases EXAFS results provide strong evidence for the structural reorganization of the support in the vicinity of the metal particles, enabling a direct bonding between metal atoms and partially reduced cations from the support, as evidenced by the detection of Rh–Ti^{*n*+}, Rh–Ta^{*n*+}, Ni–Nb^{*n*+}, and Ni–Ti^{*n*+} contributions in the EXAFS spectra.^{36–38}

CO Adsorption on Pt. Additional information regarding the state of Pt in Pt/TiO₂ and Pt/ γ -Al₂O₃ can be obtained from the FTIR spectra recorded during the adsorption and desorption of CO as a probe molecule.³⁹ No differences were observed between Pt/ γ -Al₂O₃ samples reduced in the 200–400 °C temperature range and bands observed at 2062 and 1829 cm⁻¹ can be assigned to terminal and bridging CO species adsorbed on metallic Pt, respectively (Figure 3A). The red shift observed with these samples in the terminal CO band during desorption (Figure 4A) is consistent with a decrease in the dipole–dipole coupling effect between adsorbed CO molecules due to a decrease in the CO surface coverage. In general, these data indicate that the Pt–support interactions in the Pt/ γ -Al₂O₃ sample were relatively weak and did not alter the surface properties of Pt to a noticeable extent.

In contrast, substantial differences were observed between Pt/TiO_2 samples reduced at different temperatures. More specifically, the intensities of both the linear and bridged CO bands were decreased by 40% and 70%, respectively, as the reduction temperature was increased from 300 to 500 °C, indicating a significant change in the chemisorptive properties of Pt (Figure 3B). Furthermore, no apparent shift was observed during desorption (Figure 4B), indicating the absence of any significant dipole—dipole coupling between CO molecules in these cases. Thus, the infrared data provide strong evidence for a decrease of the total amount of CO adsorbed on Pt/TiO_2 with increasing reduction temperature, which is consistent with earlier literature reports.^{3,4}

The reduction temperature of 300 °C appears to represent a critical point at which the change of Pt properties in the Pt/ TiO₂ samples takes place. At this point a substantial decrease is observed in the intensity of the band at 2076 cm^{-1} and a new band appears at 2060 cm^{-1} (Figure 3B). The appearance of this new band representing linear CO species at lower wavenumbers indicates the creation of new electron-rich Pt sites in the sample. Such an increase of the electron density of Pt results in an increase of the back-donation of the metal electrons into $2\pi^*$ antibonding orbitals of the CO molecule and a weakening of the C=O bond. The presence of electron-rich Pt sites in Pt/TiO₂ following reduction at temperatures above 300 °C suggests the existence of electronic interactions between Pt and the support in agreement with the XPS data discussed earlier. Still, however, the electronic properties of a small fraction of Pt sites remained unchanged, as indicated by the presence of a shoulder observed at the original location of the terminal CO band (i.e., 2076 cm⁻¹) (Figure 3B). These arguments are further supported by the results obtained during the desorption of CO. According to the Blyholder model³⁹ describing the interaction of CO with transition metals, an increase in the electron density of the metal does not only result in a weakening of the C=O bond, but also a strengthening of the Pt-CO bond.^{40,41} However, this model is disputed by more recent theoretical calculations, which indicate that it is possible that changes of the electron environment of transition metals may result in an increase of back-donation, but not necessarily a strengthening of the M-CO bond.42 Consistent with this prediction, binding energies of CO on various bimetallics were found to be smaller than those determined for the corresponding monometallic surfaces.^{43–46}

Our infrared data further show that when γ -Al₂O₃ was used as the support, the reduction temperature had no effect on the thermal stability of the adsorbed CO species, which can be completely removed from the Pt surface at approximately 400 °C. This result is in good agreement with similar data reported previously for Pt/ γ -Al₂O₃.²¹ In contrast, the stability of the adsorbed CO species was found to be substantially different when TiO₂ was used as the support. For example, CO adsorbed on Pt/TiO₂ samples that were previously reduced in H₂ at 200 °C can be completely removed from the surface at approximately 60 °C (Table 3). The strength of CO adsorption decreases even further on Pt/TiO₂ samples reduced in H₂ in the 300–500 °C range. Room temperature treatment in He was enough in these cases to completely remove the adsorbed CO, consistent with a very week Pt–CO bonding in these samples.

In summary, the infrared results demonstrate that supported platinum particles interact much stronger with TiO₂ than with γ -Al₂O₃. These metal—support interactions depend on the reduction temperature and led to an increase in the electron density of Pt following reduction at 300 °C or above, altering its chemisorptive properties and weakening the Pt–CO bonding.

Effect of Support on the Oxidation of CO. It has been previously suggested that the oxidation of CO proceeds through a Langmuir-Hinshelwood (LH) type mechanism,47 involving the reaction between CO molecules and oxygen atoms adsorbed on a metal surface. Alternatively, the reaction has also been proposed to proceed through an Elev-Rideal (ER) type mechanism⁴⁸ involving chemisorbed oxygen atoms and gas-phase CO. A growing database of reported experimental data in more recent years has provided additional insight and may suggest that both these kinetic models represent simplifications of a much more complex mechanism. For example, neither of these two mechanisms can account for the higher activity of catalysts prepared on easily reduced metal oxides as opposed to catalysts prepared on γ -Al₂O₃ or SiO₂. Moreover, it has been shown that preadsorbed CO (or O₂) species are not displaced by subsequent exposure to O_2 (or CO) and that the heat of adsorption of CO does not change significantly in the presence of O₂, suggesting that two different types of adsorption sites on the Pt surface are involved in the accommodation of CO and O2.49-52 Such data imply that there is no competition for the adsorption sites between CO and O₂, contradicting earlier suggestions that some adsorbed CO species must be desorbed from the metal surface to free adsorption sites for O₂.

In the case of Pt/TiO₂ it is likely that TiO₂ can participate in the catalytic process by providing highly active oxygen species. It is known that when oxygen vacancies are formed at the metal-support interface of Pt/TiO₂, oxygen from the gas phase could be dissociatively adsorbed on such deffects with one of the oxygen atoms filling the vacancy and the other being coordinated to the five-coordinate Ti⁴⁺ site as an adatom.^{33,53} Other surface species, such as molecularly adsorbed oxygen in the form of O₂⁻, can also be stable at relatively high temperatures.^{53,54} Moreover, it has been shown that the presence of Pt can stabilize O⁻ and O₃⁻ species photoformed on TiO₂.⁵⁵ Nevertheless, regardless of the nature of the oxygen species formed, one may assume that the presence of such species conveniently located at the metal support interface contributes to the higher activity of Pt/TiO₂ for the oxidation of CO.

In contrast to earlier observations,⁵⁶ our results show that among the different Pt/TiO₂ samples examined, the most active

for the oxidation of CO was the one reduced in H₂ at 400 °C (Figure 6). This sample was characterized by a reduced Pt/Ti ratio and a negative shift (by 0.4 eV) of the Pt (4f) lines (Table 2), consistent with the assumption that Pt particles in this case are partially covered by fragments of partially reduced support (TiO_x) (although it is not clear at this point whether such decoration of Pt by TiO_x takes place under CO oxidation conditions). Electronic interactions between Pt and these fragments are expected to result in an increase of the electron density on Pt and, therefore, a weakening of the CO adsorption (as already shown by the FTIR results discussed previously). Since the reaction between adsorbed CO and oxygen atoms is believed to be the rate-determining step during oxidation of CO, it is expected that the presence of weakly bonded CO and/or O2 species on the Pt surface would favor higher reaction rates, in agreement with our observations.

Reactivity of Various CO Species. Our in situ FTIR results provide valuable information regarding the reactivity of the various CO species adsorbed on the Pt surface. When freshly reduced Pt/TiO₂ and Pt/ γ -Al₂O₃ samples were exposed to the 1% CO/He flow, the intensity of the bands corresponding to the terminal and bridging CO species adsorbed on Pt was the same even when the adsorption was performed at temperatures as high as 300 °C, consistent with the high heat of CO adsorption on Pt.57 When the CO adsorption was conducted in the presence of air (Figures 8A and 8B), the CO bands for both terminal and bridging species were observed at slightly higher wavenumbers (a shift of approximately 5 cm^{-1}), signifying the presence of O₂ on the Pt surface, consistent with earlier reports.⁵¹ Furthermore, the appearance of the weak band at approximately 2121 cm⁻¹ in the spectra of both Pt/TiO₂ and Pt/ γ -Al₂O₃ samples indicates that at room temperature a small fraction of Pt⁰ sites was converted to Pt²⁺ in the CO/Air mixture.²³ It has been previously shown that Pt clusters with an average diameter of 10 Å can be completely disintegrated after exposure to O_2 at room temperature.⁶ However, the heat of adsorption of O₂ on Pt, which typically ranges between 214 and 335 kJ/mol depending on coverage,⁵⁸ can be as low as 30 kJ/mol⁵¹ in the presence of CO. Such weakly adsorbed oxygen species appear to have no significant effect on the structure of supported Pt particles, and only a small fraction of Pt²⁺ species is formed (as indicated by the 2121 cm⁻¹ band) regardless of particle size or the support used.

The in situ FTIR measurements conducted under CO oxidation conditions over both Pt/TiO₂ and Pt/ γ -Al₂O₃ (Figure 8A) indicate that the reaction between CO and oxygen was negligible at room temperature as evidenced by the presence of substantial amounts of terminal (band at 2080 cm⁻¹) and bridging (band at 1835 cm^{-1}) CO species on the Pt surface. As the temperature was increased, the intensity of both bands was decreased, indicating relatively low surface coverages at elevated temperatures due to the reaction between CO and oxygen, implying that both terminal and bridging CO species adsorbed on Pt are active in the oxidation of CO. However, the bridging CO species were less thermally stable on the Pt surface (Figure 4B) and the first to disappear from the spectra under reaction conditions, suggesting that the weakly adsorbed species may be more reactive for the oxidation of CO. At the same time, the intensity of the band at 2125 cm⁻¹ remained almost unaffected by the reaction temperature, implying that the CO species adsorbed on Pt²⁺ sites are not involved in the reaction. The catalytic and infrared data show similar trends (Figures 6 and 9) indicating that reduced samples were more active in the oxidation of CO

as compared to the oxidized ones. Furthermore, the activity of reduced samples was increased with increasing reduction temperature.

Similar behavior for the terminal and bridging CO species was observed by *in situ* FTIR on the Pt/ γ -Al₂O₃ sample (Figure 8B). Furthermore, no substantial differences were observed between Pt/ γ -Al₂O₃ samples reduced at various temperatures. Finally, no substantial differences were observed in the catalytic data (Figure 5A) obtained with these samples, suggesting that in the case of Pt/ γ -Al₂O₃ pretreatment at different conditions did not induce any metal—support interactions capable of affecting either the chemisorptive or catalytic properties of Pt.

Structural Changes of Pt/y-Al₂O₃ under CO Oxidation Conditions. The in situ FTIR results (Figure 8B) show that under reaction conditions the disappearance of the terminal and bridging CO species was accompanied by the appearance of a strong band at 2112 cm⁻¹ indicating the oxidation of Pt. This process was more noticeable with increasing reaction temperature for Pt/γ -Al₂O₃ than for Pt/TiO_2 . This difference can be attributed to differences in the Pt dispersion (Table 1) since the smaller Pt particles observed on Pt/γ -Al₂O₃ are more susceptible to oxidation. Moreover, previous literature data reported for Pt/ γ -Al₂O₃ show that at high reaction temperatures and, therefore, high CO conversions, oxygen species dominate the coverage on the Pt surface.⁵⁹ At these conditions, the majority of the oxygen species are strongly bonded to Pt due to high heats of oxygen adsorption in the absence of CO species. One would expect that such strong O_2 adsorption will mainly have an affect on the structure of small Pt particles as opposed to big ones, in agreement with our observations.

The infrared and EXAFS data reported here lead to a better understanding of the light-off curves characterizing the CO oxidation over the Pt/ γ -Al₂O₃ samples that were reduced at 200 °C or oxidized at 300 °C (Figures 5A and 5B). The inflection points observed in the light-off curves of these samples in the 216-235 °C temperature range could be explained by structural changes of Pt before and after the ignition temperature similar to what has been suggested elsewhere.⁵⁹ Reduction of Pt/y-Al₂O₃ at 200 °C leads to the formation of highly dispersed supported Pt particles having an average diameter of approximately 9 Å with nearly all the Pt atoms exposed (Table 1). Such small particles were characterized by a first-shell Pt-Pt coordination number of 4.5 at a bond distance of 2.72 Å and by a secondshell Pt-Pt coordination number of 2.2 at a bond distance of 3.91 Å (Table 5). The Pt-O contributions were observed in the spectrum at short (Pt-O_s) and long (Pt-O_l) distances of 2.13 and 2.65 Å, respectively, signifying interactions of Pt with the support, which are typical for supported metals.⁶⁰ Exposure of the sample to a CO/air mixture at 160 °C had some impact on the structure of the surface Pt species. The second-shell Pt-Pt contributions were no longer present in the spectrum, indicating some disintegration of the Pt particles under these conditions. The observed increase of the coordination number for the $Pt-O_s$ contributions to 2.0 (Table 5) may be further regarded as evidence that interactions with O2 have caused some structural changes of the metal particles. However, the degree of such changes was relatively small as the first-shell Pt-Pt coordination number remained nearly unchanged (Table 5). Thus, our EXAFS data allowed us to infer that at relatively low reaction temperatures, and therefore low CO conversions with plenty of CO present in a gas phase, O₂ as a reactant has a small impact on the structure of highly dispersed Pt particles.

Stronger changes in the value of N_{Pt-Pt} were observed when the same sample was exposed to the CO/air flow at 280 °C (Table 5). In this case, the sample was characterized by a N_{Pt-Pt} of 3.1 and by a N_{Pt-Os} of 2.8 consistent with the suggestion that Pt particles were disintegrated at these conditions to a larger extent. As a result, oxide-like Pt species were formed, as evidenced by the appearance of the characteristic band for the Pt²⁺–CO species at 2121 cm⁻¹ in the FTIR spectrum (Figure 8B). However, the EXAFS data indicate that at high reaction temperatures and high CO conversions, the surface of the catalyst resembles extremely small Pt clusters incorporating no more than 4–6 Pt atoms (Table 5). Such Pt clusters can be positively charged⁶¹ and therefore be less active for the oxidation of CO as opposed to completely reduced Pt species. This conclusion is in agreement with our catalytic data demonstrating that the reduced Pt/TiO₂ samples were more active than the oxidized ones.

It is interesting that the low- and the high-temperature features of the light-off curves characterizing the Pt/γ -Al₂O₃ after the reduction at 200 °C can be completely reproduced upon decreasing the reaction temperature, indicating the reversible nature of the suggested structural changes. We associate such reversibility with the ability of CO to reduce partially or completely oxidized Pt species formed during the course of the catalytic reaction. Such reduction presumably takes place at low reaction temperatures, while at high reaction temperatures (and therefore high CO conversions) the lack of CO in the gas phase once again leads to the partial oxidation of Pt. Similarly, when initially oxidized Pt/γ -Al₂O₃ was exposed to the CO/air mixture at room temperature, initial contact with the CO led to the partial reduction of Pt. This essentially explains why the light-off curves characterizing the oxidized Pt/y-Al₂O₃ were almost identical with those of the sample reduced at 200 °C (Figure 5B) and suggests that these two samples have a similar structure under reaction conditions.

Furthermore, the EXAFS data show that under reaction conditions the Pt–Pt bond distance in Pt/γ -Al₂O₃ was about 2.78 Å, which is 0.06 Å larger than that observed in the freshly reduced samples (Table 5). It is not quite clear at the moment why the Pt-Pt bond distance was increased under reaction conditions. If these changes were due to the oxidation of Pt by O2, the Pt-Pt contributions would be expected at a shorter distance.6 Changes in the Pt-Pt bond distance were observed previously by EXAFS when Pt-containing samples were exposed to H₂, but were not detected upon exposure to various types of hydrocarbons.⁶ On the other hand, the experimental structural parameters determined from EXAFS data indicate that the metal-metal bond distances in fully carbonylated Ru₃(CO)₁₂ or Rh₆(CO)₁₆ clusters are typically larger than those observed in corresponding decarbonylated species.⁶⁰ This allows us to suggest that under our experimental conditions the observed increase of the R_{Pt-Pt} could be explained by a possible formation of Pt carbonyl clusters with structures that cannot be precisely identified from our EXAFS data. Infrared data reported by Ichikawa et al.⁶² provide evidence for the formation of [Pt₃(CO)₆]²⁻ from H₂PtCl₆ after treatment with CO and H₂O at 50 °C, although such structural data as the Pt-Pt bond distances were not reported for this cluster. The process of the formation of Pt carbonyls could be similar to that of the formation of γ-Al₂O₃-supported Ir₄ or Ir₆ carbonyl clusters upon reductive carbonylation of mononuclear Ir species.⁶¹

Finally, the fact that an unusual shape of the light-off curves was observed only for Pt/γ -Al₂O₃ having dispersed Pt particles is consistent with the inference that only exposed metal surfaces

are vulnerable to the structural changes induced by reactants as was shown by EXAFS for Pt/γ -Al₂O₃ during the hydrogenation of alkenes.⁶

Preferential Oxidation of CO in Hydrogen-Rich Streams (**PROX**). The catalytic data of Figure 10 indicate that Pt/γ -Al₂O₃ can effectively and selectively oxidize CO in the presence of hydrogen in agreement with previous literature reports.⁶³ The results show that the CO and O₂ conversions proceed in parallel with increasing reaction temperature up to 210 °C. At that point complete conversion of both CO and O2 was reached simultaneously, yielding a selectivity of approximately 50%. At low reaction temperatures, the surface of Pt is nearly covered to saturation by CO due to the high heat of CO adsorption as compared to H₂.⁶⁴ Therefore, the lack of sufficient H₂ surface concentration is believed to be limiting the H₂ oxidation activity under these conditions. However, at higher reaction temperatures, the removal of CO from the Pt surface due to the reaction with O₂ or partial desorption creates vacant active sites capable of accommodating H_2 , and therefore, accelerating the H_2 oxidation reaction. Thus, the observed decrease in CO conversion with increasing temperature (Figure 10) leaves a very narrow window for successful operation of this catalyst in the selective oxidation of CO and requires a precise control of the reaction temperature. A simple comparison of the results obtained over the same Pt/γ -Al₂O₃ sample for the oxidation of CO in the absence (Figure 8A) and presence of H₂ (Figure 10) indicates that in the presence of H₂ the light-off curve is shifted to lower temperatures by approximately 30 °C, consistent with previous literature reports.⁶⁵ A subsequent increase of the reaction temperature led to a decrease in the CO conversion (Figure 10), consistent with the loss of O₂ due to the competing oxidation of H₂, leading to reduced selectivities at higher temperatures.66-68

When Pt/TiO₂ was reduced at 200 °C, no activity for the selective oxidation of CO was observed at low temperatures and the light-off curve obtained resembled that observed for the Pt/ γ -Al₂O₃ sample, with a delay of approximately 30 °C and a maximum CO conversion of only 62%. In contrast, when the sample was reduced at 300 °C or higher, a low-temperature activity was evident in the light-off curve, characterized by a maximum of 30% CO conversion at 70 °C (Figure 11). These results are in agreement with recent reports, illustrating the ability of Pt/TiO₂ to selectively oxidize CO in hydrogen-rich streams over a broad range of temperatures.⁶⁹ The low-temperature activity observed is directly related to the reduction temperature at which Pt/TiO₂ shows such activity.

The striking result here is that in the case of Pt/TiO₂ the lightoff curves for CO and oxygen do not resemble each other, as was observed for Pt/ γ -Al₂O₃ (Figure 10). Complete O₂ consumption, for example, is observed at 150 °C for the sample reduced at 200 and 120 °C for the samples reduced at 300 and 400 °C (Figure 11), indicating that the oxidation of H₂ to form H₂O proceeds with much higher rates over Pt/TiO₂ than over Pt/ γ -Al₂O₃. Furthermore, the oxidation of H₂ is affected by the strength of the Pt-support interactions, since the light-off curves characterizing the O₂ consumption are shifted to lower temperatures with increasing reduction temperature of Pt/TiO₂ (Figure 11).

Finally, we should point out that substantial conversion of CO with a maximum of about 62% was observed over the various Pt/TiO_2 samples in the 170–300 °C temperature range with the light-off curves in this region being insensitive to the reduction temperature (Figure 11). With no reason to believe

that the rate of hydrogen oxidation is decreased at these temperatures, the observed conversion of CO is likely related to the onset of side reactions such as methanation and/or the water-gas shift reactions.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{1}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2$$
 (2)

The results of independent kinetic measurements conducted with a 0.5% CO-45% H₂ mixture over the same catalysts indicate no substantial activity for the methanation reaction (1) at temperatures below 300 °C. This result is consistent with previous reports indicating that the activity of Pt/ γ -Al₂O₃ for CH₄ formation under PROX conditions is negligible at temperatures below 225 °C.⁷⁰ Above this temperature, the formation of methane increases slowly to a maximum of 0.025% at approximately 350 °C.⁷⁰

It is thus more likely that the water-gas shift reaction (2) is a major contributor to the observed conversions of CO in the 170-300 °C temperature range. The H₂O, which is required for the reaction to proceed, is produced in situ as the product of H₂ oxidation. The equilibrium constant reported for this reaction suggests that at aproximately 200 °C the forward reaction should be dominant in the absence of large amounts of both H_2 and CO_2 in the reaction stream.⁷¹ Indeed substantial activity for the water-gas shift reaction has been reported previously for Pt/TiO₂ in the 200-400 °C range,⁷² closely resembling our catalytic data (Figure 11). The water-gas shift reaction appears to be structure insensitive, as the turnover frequencies determined at differential conditions were essentially constant over a wide range of Pt dispersions.⁷² However, it was shown that these turnover frequencies depend strongly on the type of TiO₂ used, suggesting that the support plays an important role in this reaction.⁷² In general, the water-gas shift reaction has been described by a redox mechanism,⁷³ involving the oxidation of CO adsorbed on Pt by oxygen from the support followed by the restoration of the support surface with oxygen atoms from H₂O.⁷⁴ Alternatively, an associative mechanism has also been suggested involving the interaction of CO adsorbed on the metal surface with hydroxyls on the support leading to the formation of a formate-like intermediate, the subsequent decomposition of which results in the formation of CO2 and H₂.⁷⁵ In both cases, the support plays an important role and the function of Pt is most likely restricted to the supply of CO molecules to the metal support interface, emphasizing the bifunctional nature of the reaction. Such a scheme is consistent with our catalytic data demonstrating the lack of an effect by the reduction temperature on the CO conversion due to the water-gas shift reaction in the 170-300 °C temperature range over Pt/TiO₂ (Figure 11).

Conclusions

Platinum particles of various sizes were formed on γ -Al₂O₃ and TiO₂ from a H₂PtCl₆•6H₂O precursor following reduction in H₂ at different temperatures in the 200–400 °C range. These particles were characterized by FTIR, HRTEM, XPS, and EXAFS and their catalytic properties were examined for the oxidation of CO in the absence and presence of H₂.

When γ -Al₂O₃ was used as the support, Pt particles as small as 9–11 Å on average were formed. *In situ* FTIR data show that both the terminal and bridging CO species adsorbed on Pt can be effectively oxidized. EXAFS data further show that during the course of the CO oxidation reaction these Pt particles can undergo substantial structural changes induced by the strong adsorption of the reactants. Exposure of Pt/γ -Al₂O₃ to a CO/ air mixture at 280 °C, for example, led to partial fragmentation of the metal particles. As a result, extremely small platinum clusters incorporating no more than 4-6 metal atoms strongly interacting with the support were formed. Being exposed to O₂ under these reaction conditions, such small Pt clusters can be positively charged, and therefore, be less active for CO oxidation than fully reduced Pt. The transformation of metal clusters to these oxide-like species appeared to be reversible and mainly responsible for the inflection points observed in the light-off curves in the 215-235 °C temperature range. In contrast, exposure of Pt/γ -Al₂O₃ to the same CO/air mixture at low reaction temperatures did not result in any substantial changes in the morphology of the platinum particles, since the Pt-Pt first-shell coordination number remained almost unchanged. However, the Pt-Pt bond distance was increased due to the possible formation of Pt carbonyl species.

Platinum particles with an average diameter of approximately 26 Å were formed on the TiO₂ support. In this case, the strength of the Pt-support interactions depends mainly on the reduction temperature and can lead to an increased electron density on Pt, altering its chemisorptive properties and leading to a weakening of the Pt-CO bonding. These factors appear to promote the oxidation of CO. In addition, the higher activity of TiO₂-supported samples can also be attributed to the ability of TiO₂ to provide or stabilize highly reactive oxygen species presumably located at the metal-support interface. However, such oxygen species appear to be much more reactive toward H₂ than CO. As a result, the Pt/TiO₂ samples examined show poor selectivities for the CO oxidation under PROX conditions.

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