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# FTIR Study of Hydrogen and Carbon Monoxide Adsorption on Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub>

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The Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts submitted to low-temperature reduction (LTR, 200 °C) and high-temperature reduction (HTR, 500 °C) and exposed to hydrogen and carbon monoxide at room temperature were studied by infrared spectroscopy. There is a strong loss of transmission in the entire infrared spectra on Pt/TiO<sub>2</sub> after its exposure to hydrogen, which is related to the reducibility of the support. A typical SMSI behavior (strong metal–support interaction), such as the decrease in carbon monoxide adsorption capacity, was detected on Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> after exposure to hydrogen, even for the catalysts submitted to LTR treatment. Also a carbonyl band shift to lower wavenumber was observed on LTR-treated Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> after exposure to hydrogen. We interpreted this SMSI behavior as an electronic rather than morphological effect, which was induced by the presence of hydrogen spillover.

## Introduction

Strong metal–support interactions (SMSI) were originally reported for platinum dispersed on titania surface, indicated by reduced hydrogen adsorption capacity without a significant enlargement of metal particles.<sup>1,2</sup> During the past two decades, several studies on the metal–support interactions and their effects on catalytic properties have been published.<sup>3–11</sup> Group VIII metal particles on the reducible oxides show important differences in the catalytic activity and selectivity for hydrogenation reactions<sup>4,5,10–17</sup> when reduced at high temperatures (500 °C), compared with the unreducible supports or reduction at lower temperatures (200 °C).

The SMSI behavior has been extensively interpreted as a consequence of morphological effects.<sup>9,18–21</sup> Reducible

metal oxides such as TiO<sub>2</sub>, after high temperature reduction (HTR), undergo an expansion of the crystalline lattice due to the decreased electrostatic attractions in the ionic crystal, since titanium oxide is partially reduced forming TiO<sub>2-x</sub> species. This expansion results in a mechanism of encapsulation of metal particles, which has been described usually as a migration of TiO<sub>2-x</sub> species to the platinum surface.<sup>14,20–23</sup> However, electronic effects interpreted as a charge transfer process from the support to the dispersed metal were also discussed as a possible origin of SMSI.<sup>6,11,19–21,24–29</sup>

Other arguments such as the presence of alkali or sulfur on promoted catalysts,<sup>25,29–32</sup> as well as the formation of Pt alloys have been used to explain the SMSI behavior.<sup>20,28,34,35</sup>

Infrared spectroscopy is a useful tool for SMSI study. Several works have shown that metal–support interactions may be investigated by FTIR using probe molecules

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(1) Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 170.

(2) Tauster, S. J.; Fung, S. C. *J. Catal.* **1978**, *55*, 29.

(3) Haller, G. L.; Resasco, D. E. In *Advances in Catalysis*; Eley, D. D., Pires, H., Weisz, P. B. Eds.; Metal–Support Interaction: Group VIII Metals and Reducible Oxides. Academic Press: San Diego, CA, 1989; p 173.

(4) Sen, B.; Vannice, M. A. *J. Catal.* **1991**, *130*, 9.

(5) Sen, B.; Vannice, M. A. *J. Catal.* **1988**, *113*, 52.

(6) Chen, K.; Fan, Y.; Yan, Q. *J. Catal.* **1997**, *167*, 573.

(7) Koertz, T.; Welters, W. J. J.; van Santen, R. A. *J. Catal.* **1992**, *134*, 1.

(8) Lavalley, J. C.; Saussey, J.; Lamotte, J.; Breault, R.; Hindermann, J. P.; Kiennemann, A. *J. Phys. Chem.* **1990**, *94*, 5941.

(9) van de Loosdrecht, J.; van de Kraan, A. M.; Dillen, A. J.; Geus, J. W. *J. Catal.* **1997**, *170*, 217.

(10) Vannice, M. A. *J. Mol. Catal.* **1990**, *59*, 165.

(11) Ishihara, T.; Harada, K.; Egushi, K.; Arai, H. *J. Catal.* **1992**, *136*, 161.

(12) van de Loosdrecht, J.; van der Kraan, A. M.; van Dillen, A. J.; Geus, J. W. *J. Catal.* **1997**, *170*, 217.

(13) Vannice, M. A.; Twu, C. C.; Moon, S. H. *J. Catal.* **1983**, *79*, 70.

(14) Krishna, K. R.; Bell, A. T. *J. Catal.* **1997**, *130*, 597.

(15) Vannice, M. A.; Sen, B. *J. Catal.* **1989**, *115*, 65.

(16) Vannice, M. A.; Twu, C. C. *J. Catal.* **1983**, *82*, 213.

(17) Englisch, M.; Jentys, A.; Lercher, J. A. *J. Catal.* **1997**, *166*, 25.

(18) Tauster, S. J. *Acc. Chem. Res.* **1987**, *20*, 389.

(19) Belton, D. N.; White, J. M. *J. Phys. Chem.* **1984**, *88*, 1690.

(20) Spencer, M. S. *J. Catal.* **1985**, *93*, 216.

(21) Resasco, D. E.; Haller, G. L. *J. Catal.* **1983**, *82*, 279.

(22) Santos, J.; Phillips, J.; Dumesic, J. A. *J. Catal.* **1983**, *81*, 147.

(23) Baydal, J. P. S.; Lambert, L. M. *J. Catal.* **1991**, *130*, 173.

(24) Yoshitake, H.; Iwasawa, Y. *J. Phys. Chem.* **1992**, *96*, 1329.

(25) Tauster, S. J.; Fung, S. C.; Baker, T. K.; Horsley, J. A. *Science* **1981**, *211*, 1121.

(26) Kesraoui, S.; Oukaci, R.; Blackmond, G. *J. Catal.* **1987**, *105*, 432.

(27) Chen, B. H.; White, J. M. *J. Phys. Chem.* **1983**, *86*, 3534.

(28) Resasco, D. E.; Weber, R. S.; Sakellson, S.; McMillan, M.; Haller, G. L. *J. Phys. Chem.* **1988**, *92*, 189.

(29) Aranda, D. A. G.; Schmal, M. J. *J. Catal.* **1997**, *171*, 398.

(30) Waghay, A.; Wang, J.; Oukaci, R.; Blackmond, D. G. *J. Phys. Chem.* **1992**, *96*, 5954.

(31) Benedetti, A.; Carimati, A.; Marengo, S.; Martinengo, S.; Pinna, F.; Tessari, R.; Strukul, G.; Zerlia T.; Zanderighi, L. *J. Catal.* **1990**, *122*, 330.

(32) Kunimori, K.; Ito S.; Uchijima, T. *J. Catal.* **1991**, *130*, 662.

(33) Lin, L.; Kuntz, R. R. *Langmuir* **1992**, *8*, 870.

(34) Arai, M.; Obata, A.; Nishiyama, Y. *J. Catal.* **1997**, *166*, 115.

(35) Lamber, R.; Ekloff, G. S. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1479.

as CO and H<sub>2</sub>, reporting that HTR produces the spillover mechanism. The hydrogen spillover process occurs when the H<sub>2</sub> molecule is dissociated on the metal surface followed by the migration of the H atoms to the bulk support. The presence of atomic hydrogen produces a strong absorption in the infrared region, as observed for Ru/TiO<sub>2</sub>,<sup>36</sup> and Ru/ZnO.<sup>37</sup>

In this work, infrared spectroscopy was used to study the SMSI behavior. A decrease in the carbon monoxide adsorption capacity was detected for reducible catalysts, after reduction at low temperature (LTR). A carbonyl band shift to lower wavenumbers was observed in the presence of hydrogen, even for Pt on unreducible alumina. Under the LTR condition, the strong metal–support interactions are not expected. A typical SMSI behavior was observed by infrared spectroscopy using carbon monoxide and hydrogen as probe molecules, and the SMSI was attributed to electronic effects induced by the hydrogen spillover mechanism.

### Methods

**Synthesis of Pt/TiO<sub>2</sub>.** A solution (0.75 mL) of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (160 mg) was dropped under constant stirring on 3 g of TiO<sub>2</sub> (anatase) (P25 Degussa).<sup>1</sup> The solid was stirred for 2 h, accompanied by a drastic decrease in volume. The resulting material was dried at 110 °C for 16 h.

**Synthesis of Pt/ZrO<sub>2</sub>.** Monoclinic ZrO<sub>2</sub> was prepared by hydrolysis of ZrCl<sub>4</sub><sup>38</sup> (12 g) with distilled water (100 mL), followed by addition of ammonium hydroxide. The solid was then washed with distilled water in order to eliminate ammonium chloride and excess of ammonium hydroxide. Afterward, the resulting solid was dried at 110 °C for 4 h and calcinated in two steps, first for 4 h at 500 °C and finally at 700 °C for 4 additional hours.

A solution (1 mL) of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (212.4 mg) was dropped under constant stirring on 4 g of monoclinic ZrO<sub>2</sub>. The solid was stirred for 2 h and dried at 110 °C for 16 h.

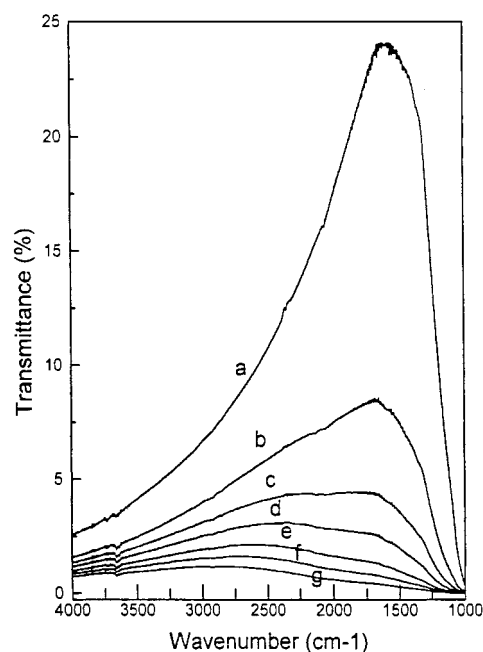
**Synthesis of Pt/Al<sub>2</sub>O<sub>3</sub>.** A solution (1 mL) of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (212.4 mg) was dropped under constant stirring on 4 g of γ-alumina (Aldrich). The solid was stirred for 2 h and dried at 110 °C for 16 h.

**Reductive Thermal Treatment.** Self-supporting disks of TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and the corresponding Pt catalysts, with an area of 5 cm<sup>2</sup> weighting 50 mg each were prepared, heated to 200 °C under vacuum (10<sup>-5</sup> Torr) (1 Torr = 133.3 Nm<sup>-2</sup>) for 1 h, and exposed to 200 Torr of oxygen for 1 h at 200 °C. The oxygen was pumped off (10<sup>-5</sup> Torr) for 1 h at 300 °C. After that, the materials were exposed to 200 Torr of hydrogen at 200 °C (LTR) or 500 °C (HTR) for 1 h, and finally degassed at 300 °C for 1 h under vacuum.

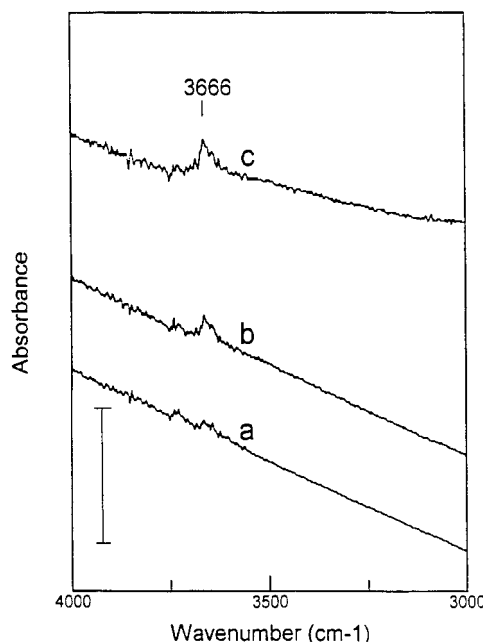
**IR Analysis.** The self-supporting disks of materials were analyzed in situ in the infrared region after LTR and HTR treatments using a Bomem FTIR spectrometer, model MB-102. The IR cell was connected to a greaseless vacuum line through which carbon monoxide, hydrogen, and oxygen could be admitted to the system under controlled pressure. The spectra were obtained with a resolution of 4 cm<sup>-1</sup>, with 256 scans for the material submitted to LTR treatment and 1024 scans for the material to which a HTR treatment was applied.

### Results

**Hydrogen Adsorption on Catalysts after the LTR Treatment.** The infrared spectra of LTR-treated Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> exposed to different pressures of hydrogen at room temperature are shown in Figures 1–4. A drastic decrease in the transmittance for Pt/TiO<sub>2</sub> can be observed under 5 Torr of H<sub>2</sub> (Figure 1b). On the other hand, an increase of the TiO–H band area was observed



**Figure 1.** Transmittance spectra of LTR-treated Pt/TiO<sub>2</sub>, followed by (a) degassing at 300 °C; (b) 5 Torr H<sub>2</sub>; (c) 10 Torr H<sub>2</sub>; (d) 20 Torr H<sub>2</sub>; (e) 50 Torr H<sub>2</sub>; (f) 100 Torr H<sub>2</sub>; (g) 200 Torr H<sub>2</sub>.



**Figure 2.** Absorbance spectrum of LTR-treated Pt/TiO<sub>2</sub>, followed by (a) degassing at 300 °C; (b) 5 Torr H<sub>2</sub>; (c) 200 Torr H<sub>2</sub>. The bar value is 0.4.

in the OH stretching region in the presence of H<sub>2</sub> (see Figure 2). For Pt/ZrO<sub>2</sub> the decrease in the transmittance was lower than for Pt/TiO<sub>2</sub> (see Figure 3) and for Pt/Al<sub>2</sub>O<sub>3</sub> the transmittance was insignificant until ca. 100 Torr of hydrogen (Figure 4). At this point it is worthwhile to note that the order of decrease in transmittance is correlated with the reducibility of the support.

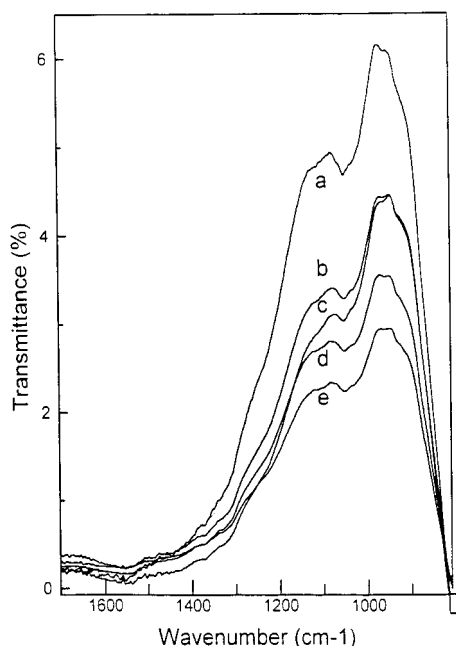
This effect was not been observed in the infrared spectra of the supports TiO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> under the same conditions. The presence of platinum on the surface is a determinant for this loss of transmission.

**HTR Treatment.** The infrared spectra of HTR-treated Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> are shown in Figures 5–7.

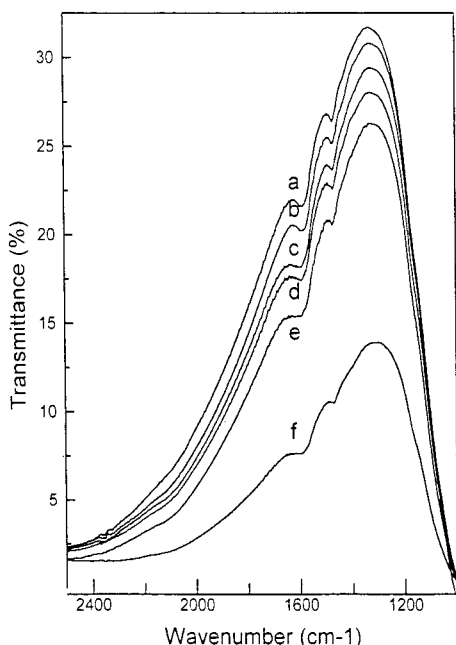
(36) Bond, G. C.; Guglielminotti, E. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 979.

(37) Guglielminotti, E.; Bocuzzi, F.; Ghiotti, G.; Chiorino, A. *Surf. Sci.* **1987**, *189–190*, 331.

(38) Sato, T.; Ozawa, F.; Nakamura, T.; Watanabe, H.; Ikoma, S. *Thermochim. Acta* **1979**, *34*, 211.



**Figure 3.** Transmittance spectra of LTR-treated Pt/ZrO<sub>2</sub>, followed by (a) degassing at 300 °C; (b) 10 Torr H<sub>2</sub>; (c) 20 Torr H<sub>2</sub>; (d) 50 Torr H<sub>2</sub>; e) 100 Torr H<sub>2</sub>.

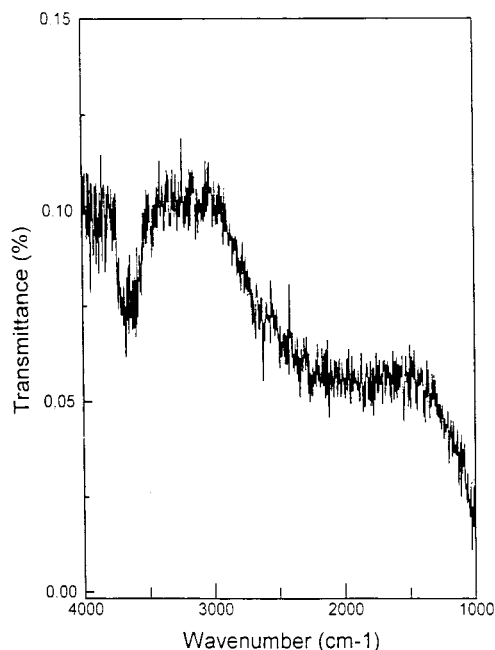


**Figure 4.** Transmittance spectra of LTR-treated Pt/Al<sub>2</sub>O<sub>3</sub>, followed by (a) degassing at 300 °C; (b) 10 Torr H<sub>2</sub>; (c) 30 Torr H<sub>2</sub>; (d) 50 Torr H<sub>2</sub>; e) 110 Torr H<sub>2</sub>; f) 200 Torr H<sub>2</sub>.

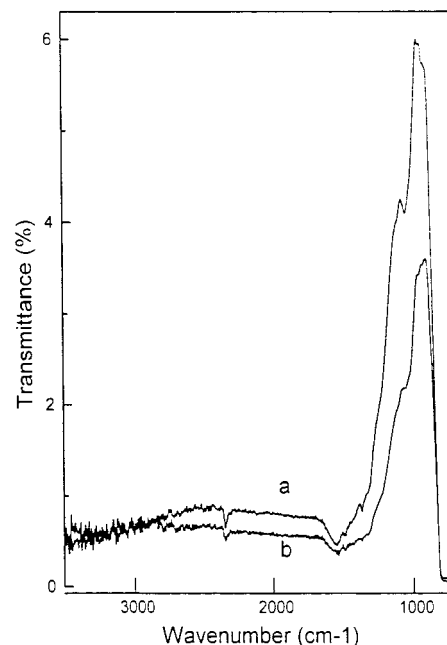
The spectrum of HTR-treated Pt/TiO<sub>2</sub> (Figure 5) shows a strong decrease in total transmittance (ca. 250 times) when compared to the LTR-treated (Figure 1a). The loss of transmission for HTR- as compared to LTR-treated Pt/ZrO<sub>2</sub> is smaller than in the previous case (see Figure 6), while for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the decrease in transmittance was negligible after HTR treatment (Figure 7).

#### Adsorption of Carbon Monoxide on the Catalysts.

The spectrum of the LTR-treated Pt/TiO<sub>2</sub> exposed to 10 Torr of carbon monoxide is shown in Figure 8a. The band at 2087 cm<sup>-1</sup> was assigned to the carbonyl stretching of linear CO coordinated to Pt particles,<sup>26,39</sup> and the band at 1860 cm<sup>-1</sup> was attributed to the  $\mu$ -CO species,<sup>26,40</sup> while the band at 2186 cm<sup>-1</sup> was assigned to carbon monoxide physically adsorbed<sup>40</sup> or coordinated to Pt ions.<sup>39</sup> This



**Figure 5.** Pt/TiO<sub>2</sub> spectrum after HTR treatment.



**Figure 6.** Spectra of Pt/ZrO<sub>2</sub>: (a) after LTR treatment; (b) after HTR treatment.

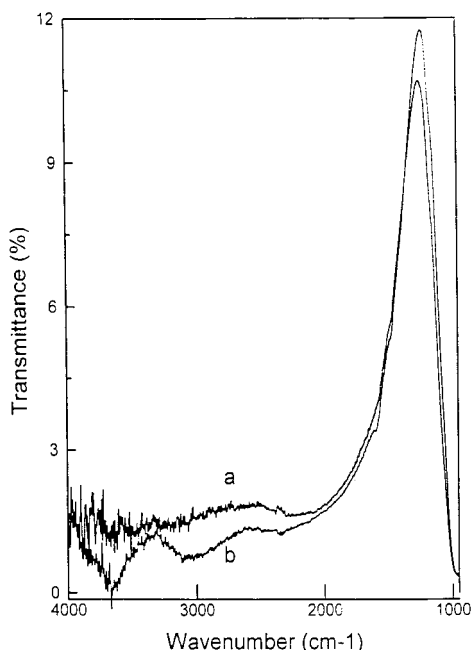
absorption can also be assigned to carbon monoxide coordinated to reduced titanium, since this band is also present in the spectrum of CO on reduced TiO<sub>2</sub>.

The spectrum of HTR-treated Pt/TiO<sub>2</sub> under 10 Torr of carbon monoxide is shown in Figure 8b. Three carbonyl bands of coordinated carbon monoxide were detected. The strong band at 2082 cm<sup>-1</sup> was assigned to carbon monoxide linearly adsorbed on Pt particles. Two very weak bands, at 1853 and 2186 cm<sup>-1</sup> were also observed and assigned to  $\mu$ -CO on Pt particles and carbon monoxide coordinated on reduced titanium, respectively.

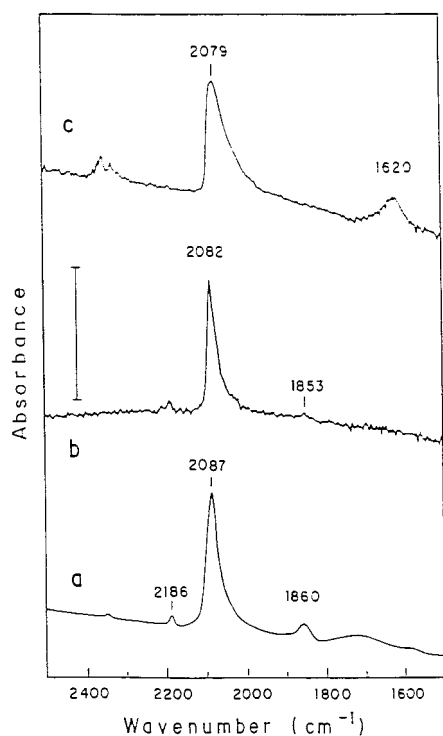
The spectrum of LTR-treated Pt/TiO<sub>2</sub> submitted simultaneously to carbon monoxide (10 Torr) and hydrogen

(39) Stakheev, A. Y.; Shpiro, E. S.; Tkachenko, O. P.; Jaeger, N. I.; Eklof, G. S. *J. Catal.* **1997**, *169*, 382.

(40) Gupta, N. M.; Londhe, V. P.; Kamble, V. S. *J. Catal.* **1997**, *169*, 423.

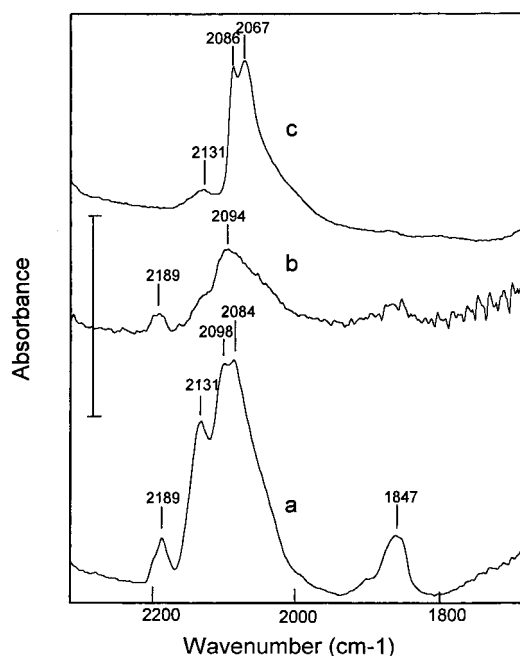


**Figure 7.** Spectra of Pt/Al<sub>2</sub>O<sub>3</sub>: (a) after LTR treatment; (b) after HTR treatment.



**Figure 8.** Spectra of Pt/TiO<sub>2</sub> exposed to 10 Torr of carbon monoxide: (a) after LTR treatment; (b) after HTR treatment; (c) contacted with 100 Torr of hydrogen after LTR treatment. The bar value is 1.3 for spectrum a, 0.6 for spectrum b, and 0.3 for spectrum c.

(100 Torr), (Figure 8c) shows only the stretching band of linear carbonyl species, at 2079 cm<sup>-1</sup>. Under these conditions the spectrum shows a broad band at 1620 cm<sup>-1</sup>. This band was assigned to the bending of H—O—H,<sup>41,42</sup> indicating the appearance of water in the solid, which has been previously reported.<sup>36,43–46</sup>



**Figure 9.** Spectra of Pt/ZrO<sub>2</sub> exposed to 10 Torr of carbon monoxide: (a) after LTR treatment; (b) after HTR treatment; (c) contacted with 100 Torr of hydrogen after LTR treatment. The bar value is 0.5.

The spectra of LTR- and HTR-treated Pt/ZrO<sub>2</sub> exposed to carbon monoxide are shown in Figure 9. Spectrum 9a for the LTR-treated sample exhibits a broad band at ca. 2100 cm<sup>-1</sup> of linear carbonyl bonded to Pt metal particles. In this broad envelope three bands might be noticed, at 2131, 2098, and 2084 cm<sup>-1</sup>. The last band can be assigned to linear carbonyl, but the two other bands can be interpreted as two kinds of species. The first is the dicarbonyl formed on monatomic platinum. Similar observations were made for platinum<sup>39,47</sup> and palladium<sup>48</sup> dispersed on zeolites, and ruthenium<sup>40</sup> and rhodium<sup>49</sup> dispersed on titania. The spectra show two bands in the dicarbonyl form with an angle of 90°. The second is the multicarbonyl species such as Pt<sup>x+</sup>(CO)<sub>n</sub><sup>36,46</sup> where the metal is partially oxidized forming Me<sup>x+</sup>(CO)<sub>3</sub>. In Figure 9a the band at 1847 cm<sup>-1</sup> is due to  $\mu$ -CO and the band at higher wavenumbers (2189 cm<sup>-1</sup>) has two interpretations: carbon monoxide physically adsorbed<sup>40</sup> or coordinated on Pt ions.<sup>39</sup> This band is absent on the Pt-free zirconia.

Figure 9b shows a broad band at ca. 2094 cm<sup>-1</sup> in the spectrum of HTR-treated Pt/ZrO<sub>2</sub> and exposed to carbon monoxide. The presence of dicarbonyl species is not clear, but there is an absorption at 2130 cm<sup>-1</sup> that can be assigned to the presence of dicarbonyl on monatomic platinum even after HTR treatment. The band of bridging carbon monoxide (ca. 1850 cm<sup>-1</sup>) and the band at 2189 cm<sup>-1</sup>, assigned to carbon monoxide physically adsorbed<sup>40</sup> or coordinated to Pt ions,<sup>39</sup> are also observed.

The spectrum of LTR-treated Pt/ZrO<sub>2</sub> submitted simultaneously to carbon monoxide and hydrogen (Figure

(44) Cavanagh, R. R.; Yates, J. T. *J. Catal.* **1981**, *68*, 22.

(45) Tanaka, K.; White, J. M. *J. Catal.* **1983**, *79*, 81.

(46) Robins, J. L. *J. Catal.* **1989**, *115*, 120.

(47) Zholobenko, V. L.; Lei, G.-D.; Carvill, B. T.; Lerner, B. A.; Sachtler, W. M. H. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 233.

(48) Xu, L.; Zhang, Z.; Sachtler, W. M. H. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2291.

(49) Evans, J.; Hayden, B.; Mosselmans, F.; Murray, A. *J. Am. Chem. Soc.* **1992**, *114*, 6912.

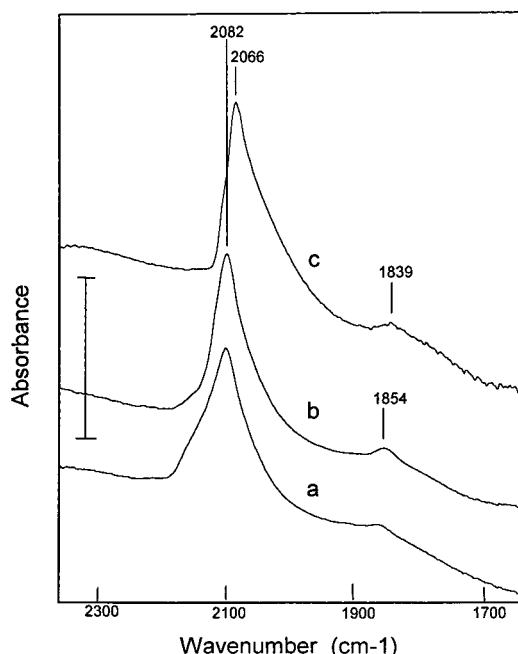
(50) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(41) Wood, D. L.; Rabinovich, E. M. *Appl. Spectrosc.* **1989**, *43*, 263.

(42) Benvenuti, E. V.; Costa, T. H.; Gallas, M.; Jornada, J. *J. Non-Cryst. Solids* **1997**, *220*, 195.

(43) Apple, T. M.; Dybowski, C. *J. Catal.* **1981**, *71*, 316.





**Figure 10.** Spectra of Pt/Al<sub>2</sub>O<sub>3</sub> exposed to 10 Torr of carbon monoxide: (a) after LTR treatment; (b) after HTR treatment; (c) contacted with 100 Torr of hydrogen after LTR treatment. The bar value is 0.5.

9c) shows both linear and dicarbonyl species, but the bands due to bridge carbonyl and the band at higher frequency have vanished. A similar behavior was observed for platinum supported on titania (Figure 8c).

The spectra of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst exposed to carbon monoxide are shown in Figure 10. For LTR and HTR treatment (Figures 10a and 10b), the spectra are very similar showing a band corresponding to the linear carbonyl at 2082 cm<sup>-1</sup> and a band of bridging  $\mu$ -CO at 1854 cm<sup>-1</sup>. When the LTR-treated Pt/Al<sub>2</sub>O<sub>3</sub> is exposed to carbon monoxide and hydrogen simultaneously (Figure 10c), the spectrum shows the same carbonyl species, but a band shift to lower wavenumbers is evident, to 2066 and 1839 cm<sup>-1</sup> for linear and bridging carbonyl, respectively.

## Discussion

**Hydrogen Adsorption on Catalysts Submitted to LTR Treatment.** A strong loss of transmission in the total infrared spectrum was observed for LTR-treated Pt/TiO<sub>2</sub> after exposure to hydrogen (Figure 1). This effect has already been observed for Ru/TiO<sub>2</sub><sup>36</sup> and Ru/ZnO.<sup>37</sup> The transmission loss might be interpreted as absorption by electronic defects on the microcrystalline level, considering that these electronic changes in the solid structure might be a consequence of hydrogen atom spillover from the metal to the support.<sup>51–54</sup> A change of the Fermi energy level of the metal under the hydrogen should be considered since the platinum can absorb large quantities of molecular hydrogen. However the spillover mechanism is also supported by the spectra of Figure 2. The stretching band area of TiO–H at 3666 cm<sup>-1</sup> increases after admitting hydrogen into the cell. This is evidence of hydrogen atoms in the metal–support interface whose presence can only be justified by the spillover mechanism.

The presence of hydrogen in the bulk, as titanium hydrides and Ti–H–Pt,<sup>55</sup> causes the disappearance of the TiO<sub>2</sub> multiphonon band and can be ascribed to phonon–plasmon coupling effects that might account for the strong infrared absorption. This effect has also been observed for ZnO.<sup>56,37</sup> Reducible supports, such as TiO<sub>2</sub>, have Schottky defects and n-type semiconductive properties.<sup>57,58</sup> The reduction of monoclinic zirconia is known<sup>59</sup> to generate Zr<sup>3+</sup> centers; thus the spectral features of reduced TiO<sub>2</sub> and ZrO<sub>2</sub> (Figures 1 and 3) can be compared to those of ZnO. Alumina is an unreducible support, thus Pt/Al<sub>2</sub>O<sub>3</sub> shows negligible infrared absorption effects up to 100 Torr of hydrogen (Figure 4), although when it was exposed to 200 Torr of hydrogen a considerable decrease in transmittance was observed. However, the spillover effect has been detected for Pt/Al<sub>2</sub>O<sub>3</sub>,<sup>60,61</sup> and reduction at temperatures higher than 500 °C produces a decrease in hydrogen adsorption capacity.<sup>51</sup> Therefore, the infrared absorption increases with the reducibility of the support.

The original transmittance in the spectra obtained before exposing the materials to hydrogen was reproduced after heating the solids to 300 °C under vacuum (10<sup>-5</sup> Torr) for 1 h. Under these conditions, the hydrogen should be completely desorbed.

**HTR Treatment.** The infrared absorption of materials following the HTR treatment increases with reducibility. The infrared absorption after HTR treatment is quite strong for Pt/TiO<sub>2</sub> (Figure 5), much less significant for Pt/ZrO<sub>2</sub> (Figure 6), and almost negligible for Pt on unreducible alumina (Figure 7). The infrared absorption can be interpreted as having the same origin as other similar effects such as for LTR treatment on Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> after hydrogen chemisorption at room temperature. However, the TiO–H stretching band area in the spectrum obtained after HTR treatment (Figure 5) is 13 times larger than that obtained after LTR treatment followed by hydrogen admission (see Figure 2). Therefore, after HTR treatment the spillover mechanism is more pronounced.

Thermal treatment under vacuum does not restore the original transmittance, as observed for catalysts exposed to hydrogen after LTR treatment. The original characteristics were only restored after oxidation (300 Torr of oxygen) at 300 °C for 1 h. Similar behavior was observed for Ru/TiO<sub>2</sub>.<sup>36</sup>

**Adsorption of Carbon Monoxide.** Table 1 shows the areas of the carbonyl stretching bands for catalysts exposed to CO after LTR and HTR treatments and exposed to CO and H<sub>2</sub> after LTR treatment. For Pt/Al<sub>2</sub>O<sub>3</sub> the areas of linear carbonyl and  $\mu$ -CO bands are almost constant. For Pt on reducible supports, the areas of the carbonyl stretching band, after HTR treatment, undergo a strong decrease when compared to the same bands after LTR treatment. This effect was more pronounced for titania (see Table 1) which is also more reducible. This band area reduction after HTR treatment is an indication of the decrease in carbon monoxide adsorption capacity due to metal support interactions. The SMSI effect produces a

(55) Elipse, A. R. G.; Fernandez, A.; Espinos, J. P.; Munuera, G. *J. Catal.* **1991**, 132, 51.

(56) Bocuzzi, F.; Morterra, C.; Scala, R.; Zecchina, A. *J. Chem. Soc., Faraday Trans. 2* **1981**, 77, 2059.

(57) Ioannides, T.; Verykios, X. E. *J. Catal.* **1996**, 161, 560.

(58) Goodenough, J. B. In *Progress in Solid State Chemistry*; Reiss, H. Ed. Oxford University Press: Oxford, UK, 1971; Vol 5; p 344.

(59) Morterra, C.; Giamello, E.; Orto, L.; Volante, M. *J. Phys. Chem.* **1990**, 94, 3111.

(60) Aparicio, P. F.; Ruiz, A. G.; Ramos, I. R. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 3563.

(61) Miller, J. T.; Meyers, B. L.; Modica, F. S.; Lane, G. S.; Vaarkamp, M.; Koningsberger, D. C. *J. Catal.* **1993**, 143, 395.

(51) Vaarkamp, M.; Miller, J. T.; Modica, F. S.; Koningsberger, D. C. *J. Catal.* **1996**, 163, 294.

(52) Chen, B.; Falconer, J. L. *J. Catal.* **1992**, 134, 737.

(53) Clewley, J. D.; Lynch, J. F.; Flanagan, T. B. *J. Catal.* **1975**, 36, 291.

(54) Lambert, J. F.; Poncelet, G.; Fripiat, T. J. *Acta Chim. Hungarica* **1987**, 124, 121.

**Table 1. Area of Carbonyl Stretching Band**

treatment <sup>a</sup>	Pt/TiO <sub>2</sub> (cm <sup>-1</sup> × abs)		Pt/ZrO <sub>2</sub> (cm <sup>-1</sup> × abs)		Pt/Al <sub>2</sub> O <sub>3</sub> (cm <sup>-1</sup> × abs)	
	linear	μ-CO	linear	μ-CO	linear	μ-CO
LTR	63.2	5.4	94.0	9.4	42.3	3
HTR	19.5	1	35.6	2.5	39.2	4
LTR (H <sub>2</sub> ) <sup>b</sup>	12.5	—	27.4	—	37.5	4

<sup>a</sup> Reductive thermal treatment under 200 Torr of hydrogen (LTR = 200 °C; HTR = 500 °C), in contact with 10 Torr of carbon monoxide.

<sup>b</sup> After LTR treatment the catalysts were exposed to 10 Torr of carbon monoxide and 100 Torr of hydrogen.

decrease in the carbon monoxide adsorption capacity as described elsewhere.<sup>1,14,25,62,63</sup> There is no decrease in the CO adsorption capacity for unreducible alumina.

An interesting behavior has been observed when the areas of the carbonyl stretching band were calculated from the spectra obtained after the catalysts were LTR treated and then simultaneously exposed to carbon monoxide and hydrogen. When carbon monoxide (10 Torr) and hydrogen (100 Torr) are introduced simultaneously into the cell, a decreased CO adsorption was observed, and this decreased adsorption is more pronounced than after HTR treatment (see Table 1). Again, the Pt/Al<sub>2</sub>O<sub>3</sub> does not show significant decrease in the carbon monoxide adsorption capacity, since the alumina is an unreducible support, and will not show SMSI effects.

The carbon monoxide adsorption capacity decreases with the SMSI effect. However, the SMSI effect has been reported only after HTR treatment. In this work, similar SMSI effects were also detected after LTR treatment.

The spectra taken after HTR treatment (SMSI effect present) for Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> show the dominance of adsorbed linear carbon monoxide (see Figures 8 and 9 and Table 1). The same behavior was observed for Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> treated by LTR and exposed to carbon monoxide in the presence of hydrogen at room temperature, although at LTR treatment the SMSI effects should not appear. Again, evidence of SMSI behavior was detected at low temperature reduction.

This interpretation is also supported by infrared analysis of the LTR-treated materials exposed to hydrogen at room temperature followed by LTR treatment (Figures 1 and 3), where strong absorptions were observed, similar to the results obtained after HTR treatment (Figures 5 and 6).

There is another important aspect of the spectra of LTR-treated Pt/TiO<sub>2</sub>, Pt/ZrO<sub>2</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub> catalyst treated by LTR and simultaneously exposed to carbon monoxide (10 Torr) and hydrogen (100 Torr), at room temperature. The stretching bands of carbonyl undergo a pronounced shift to lower wavenumbers, even for Pt on the unreducible alumina support (Figures 8c, 9c, and 10c). The catalysts treated by HTR show this band shift,<sup>39,40</sup> and this has been associated with metal particle size. However, this is not expected for catalysts reduced at low temperatures (LTR), or for alumina, which represents a typical unreducible support.

The band shift of the linear CO stretching to lower wavenumber observed on Pt/Al<sub>2</sub>O<sub>3</sub>, when exposed to carbon monoxide and hydrogen has been recently reported,<sup>64</sup> and interpreted as a consequence of carbon monoxide dispersion produced by the presence of hydrogen. Dilution of carbon monoxide avoids the dipole–dipole

coupling between adjacent CO molecules.<sup>36,65,66</sup> However, in this work, the band shift to lower wavenumber was also observed for bridging CO (see Figure 10). The band shift for linear and bridging carbon monoxide are very similar, 16 cm<sup>-1</sup> and 15 cm<sup>-1</sup>, respectively. In this case, the argument of carbon monoxide dilution does not hold, since dipole–dipole coupling is not important for the distant bridging carbon monoxide species.

The spillover mechanism and the SMSI effect has already been detected for Pt/Al<sub>2</sub>O<sub>3</sub> when reduced at temperatures higher than 500 °C.<sup>51,60,61</sup> In this work the hydrogen spillover mechanism was also detected for Pt/Al<sub>2</sub>O<sub>3</sub> treated by LTR in the presence of 200 Torr of hydrogen at room temperature (Figure 3f). Therefore, the band shift can be interpreted by taking into account the increase in electronic density in the d subshell of platinum, produced by the presence of hydrogen. The increase in electronic density might promote a stronger back-bonded platinum–carbonyl. The changes in electronic density on the d subshell have been used before to explain the SMSI behavior.<sup>11,24–26,29</sup> Thus the electronic effects were induced by the presence of hydrogen at room temperature, also for LTR-treated Pt/Al<sub>2</sub>O<sub>3</sub>.

### Further Discussion

The reducibility of the support increases the SMSI effect, including the decrease in the hydrogen and carbon monoxide adsorption capacity. In this work, Pt on the reducible titania and zirconia catalysts show a reduced carbon monoxide adsorption capacity after a HTR treatment (SMSI effect present). A similar behavior could be observed for LTR treatment (SMSI effect not expected), in the presence of hydrogen. Several works have revealed that the SMSI effect and the decrease in the hydrogen and carbon monoxide adsorption capacity are a consequence of the encapsulation effect,<sup>6,9,14,19–23</sup> which cannot be invoked here, since this decrease in adsorption capacity was detected after LTR treatment. These results suggest that the low capacity of adsorption might be a consequence of support saturation by hydrogen. The hydrogen can migrate to the reducible support by a spillover mechanism,<sup>10,25,51,52,55</sup> and this effect could be detected even at room temperature. Tauster et al.<sup>25</sup> have mentioned the possibility that strongly bonded hydrogen cannot be removed by degassing. Thus, the presumable saturation of the bulk with hydrogen produced by the HTR, on reducible supports, and the difficulties in desorbing this hydrogen, might be responsible for the low chemisorption effects.

### Conclusions

Hydrogen migrates to the bulk of catalysts treated by LTR. This migration results in a strong absorption in the infrared region and is dependent on the hydrogen pressure. The same behavior can be obtained when Pt on reducible oxide catalysts are treated by HTR.

A decrease on the carbon monoxide adsorption capacity occurs for Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> catalysts after HTR treatment as expected for Pt on reducible supports. However, the decrease in the carbon monoxide adsorption capacity is also observed for Pt/TiO<sub>2</sub> and Pt/ZrO<sub>2</sub> catalysts after LTR treatment in the presence of hydrogen. Therefore, a typical SMSI behavior was also detected after LTR treatment.

The electronic effects evidenced by the carbonyl band shifts to lower wavenumbers can be caused by LTR

(62) Vannice, M. A.; Wang, S.; Moon, S. H. *J. Catal.* **1981**, *71*, 152.

(63) Bonneviot, L.; Haller, G. L. *J. Catal.* **1991**, *130*, 359.

(64) de Ménorval, L.-C.; Chaqroune, A.; Coq, B.; Figueras, F. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3715.

(65) Primet, M. *J. Catal.* **1984**, *88*, 273.

(66) Stoop, F.; Toolenaar, J. C. M.; Ponc, V. *J. Catal.* **1982**, *73*, 50.

treatment under the presence of hydrogen even for Pt/Al<sub>2</sub>O<sub>3</sub>, and it was not induced by thermal treatment at higher temperatures.

This work suggests that the SMSI behavior observed as a decrease in the carbon monoxide adsorption capacity and carbonyl band shifts to lower wavenumbers, is a consequence of hydrogen presence on the support, possibly in the metal–support interface, which can promote electronic effects.

Hydrogen spillover increases with support reducibility, but can occur even for Pt on an unreducible alumina support.

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