# Pt-Co/SiO<sub>2</sub> Bimetallic Planar Model Catalysts for Selective Hydrogenation of Crotonaldehyde

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Surface science models of silica-supported Pt–Co bimetallic catalysts with various Pt/Co ratios have been successfully prepared using the spin-coating technique. Platinum and cobalt loadings on a series of silica-supported model catalysts were quantified by Rutherford backscattering spectrometry. Atomic force microscopy images indicate that flattish layerlike structures were obtained in all cases. The electronic state of Co and Pt was investigated using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). NEXAFS shows that cobalt is mainly forming octahedrally coordinated  $Co^{2+}$  species in the unreduced catalysts. The formation of the active phase has been investigated by XPS and "in situ" soft X-ray absorption spectroscopy (XAS). The NEXAFS measurements performed under 1-2 mbar of H<sub>2</sub> reveal that cobalt is fully reduced to Co<sup>0</sup> at relatively low temperature in bimetallic catalysts and reveal a decrease of the electron density of Co as the Pt/(Pt + Co) ratio increases, indicating the formation of alloyed bimetallic particles. This is also supported by XPS measurements. The crotonaldehyde hydrogenation has been studied on planar surface science model catalyst under diffusion-limitation-free conditions in gas phase at atmospheric pressure and temperatures between 100 and 150 °C. The addition of Co significantly improved the selectivity toward crotyl alcohol. This improvement is correlated with the electronic properties of the active phase.

## Introduction

Bimetallic catalysts constitute one of the most promising classes of catalysts, with wide application not only within the petrochemical industry (for a variety of reactions such as reforming, hydrogenation reactions and dehydrogenation of lower alkanes) but also in the fine chemical industry. The ability of a less noble metal to promote the catalytic properties of supported noble-metal-based catalysts has been known for decades.<sup>1,2</sup> The beneficial effect of adding a second metal has usually been attributed to either a geometric effect, the so-called ensemble effect, or to an electronic effect, the so-called ligand effect.<sup>1,2</sup> However, their relative importance is still under debate, and both effects were recently discussed in detail.<sup>3</sup> Obviously, it is essential that both metals be closely associated forming bimetallic clusters or particles rather than separated particles spread over the support surface.

One of the most promising applications of these bimetallic systems is the development of next-generation bimetallic nanocluster catalysts for ultraselective hydrogenation processes. Hydrogenation reactions are involved in large-scale processes in refining and petrochemical industries but also in the synthesis of a large number of fine chemicals. Particularly, the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes to produce unsaturated alcohols is the key step to produce flavors, fragrances and

pharmaceuticals.<sup>4-6</sup> It is well-known that supported metallic catalysts based on noble metals are very effective but poorly selective catalysts for hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes since the hydrogenation of the C=C double bond is both kinetically and thermodynamically favored.<sup>7,8</sup> Therefore, research efforts in this field were mainly focused on improving the selectivity to the unsaturated alcohol. In a recent review, Gallezot and Richard<sup>5</sup> summarized the main effects that can increase the selectivity of supported group VIII monometallic catalysts toward the unsaturated alcohol. In short, they reported that particle size and support effects as well as the addition of a second metal play a key role in determining the catalyst selectivity. It has been proposed that the porous structure of zeolitic supports might increase the selectivity by favoring C= O adsorption through geometric constraints of the porous structure and that metal support interactions (SMSI) could create new and more selective catalytic sites. Electronic ligand effects have also been invoked to explain selectivity enhancements in bimetallic systems. However, the types of the association between the two metals and the valence state of the second metal are very diverse and often poorly understood.

Catalyst property/reactivity relationships for high-surface-area supported catalysts have been widely investigated. Although these catalysts provide a good approximation of the industrial catalytic system, they are sufficiently complex that the understanding of the catalytic process at molecular level can be hardly achieved without supplemental investigations using simplified "model" systems. Obviously, all of the effects mentioned above can be simultaneously present on these high surface area catalysts, thereby adding an extra level of complexity. As metal

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particles are mainly located inside of the pores in high surface area catalysts, these systems are normally poorly characterized and some of the active sites may be inaccessible to certain characterization techniques. It is very difficult, therefore, to established structure/activity relationships on these catalytic systems. Hence, to elucidate the structural/electronic characteristics of the active sites and the structure-catalytic performance relationship, characterization and catalytic studies on welldefined model surfaces are imperative.

In the past, model catalysts usually implied single-crystals or thin films. These systems have been outstanding in unraveling many important questions in catalysis.9 However, most of the industrial catalytic systems involve supported catalysts, where the oxide carriers play a crucial role in determining the structure/ reactivity of the active phase. Obviously, the effect of the support was missed on these model catalysts. A surface science model of supported catalysts can be used to bridge the gap between supported "real-world" catalysts and single crystal surface science systems. Model catalysts, consisting of a planar conducting substrate with a thin oxide layer on top of which the active phase is deposited, have been successfully applied in catalysis research.9 One of the most important advantages of these systems derives from the fact that the full potential of surface science techniques can be used to obtain a detailed electronic/structural characterization of the active phase. In previous papers, we have shown that these planar model systems can be successfully applied to obtain more insight into the formation of the active phases for realistic HDS catalysts.<sup>10-13</sup> Another important advantage of planar model catalysts is the absence of pores, excluding effects of internal mass transfer limitations on the chemical kinetics. Thus, catalytic measurements can be performed under essentially diffusion-limitationfree conditions. Recently, we have demonstrated that kinetic studies can be performed on these planar model catalysts.<sup>14</sup>

Furthermore, because the physical-chemical characterization is performed on the same particles that are also responsible for the catalytic process, one can unequivocally relate structural/ electronic properties and surface composition to catalytic behavior, which is usually difficult for high surface area catalysts. Thus, the ultimate goal is to use bimetallic flat model catalysts to establish an unequivocal correlation between the structural/electronic properties and the catalytic behavior. In this contribution we explore the usefulness of these bimetallic planar model systems for the investigation of catalyst propertyreactivity relationships in the selective hydrogenation of crotonaldehyde.

## **Experimental Section**

**Catalyst Preparation.** Pt–Co/SiO<sub>2</sub> bimetallic planar model catalysts, consisting of a Si(100) wafer covered by a thin layer of SiO<sub>2</sub> as a support, were prepared by the spin-coating technique as previously described.<sup>10–13</sup> Planar SiO<sub>2</sub> model supports were prepared by oxidizing a Si(100) single-crystal wafer in air at 750 °C for 24 h. After calcination the wafers were cleaned in a H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OH (3/2 v/v) solution at 65 °C, and then the surface was hydroxylated in boiling water for 20–30 min. Subsequently, these model supports were spin-coated in a nitrogen atmosphere at 2800 rpm with an aqueous solution containing [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> (Aldrich, 99.99%) and Co(NO<sub>3</sub>)<sub>2</sub>• 6H<sub>2</sub>O (Merck, p.a.), with varying Pt/Co atomic ratios. The concentrations of the precursor solutions were adjusted to result in a total (Pt + Co) metal loading of 6 at/nm<sup>2</sup>. After spin-coating the samples were calcined in flowing air at 400 °C during 1 h.

Rutherford Backscattering Spectrometry (RBS). The Pt and Co coverage of the samples was determined quantitatively with high-resolution RBS,<sup>15</sup> using 2 MeV He<sup>+</sup> ions. The He beam hits the sample surface at near normal incidence, such that the beam was aligned with the (100) channel direction of the Si substrate. The detector was at 10° to the sample surface (scattering angle 100°). This grazing exit angle, together with the low overall count rate inherent to the channeling condition, reduced the risk of pile-up (coincident pulses) to a negligible level. With an applied total ion dose of at least 150 $\mu$ C, the quantitative results for Pt and Co are estimated to be accurate within 5%.

Atomic Force Microscopy (AFM). Atomic force microscopy (AFM) was performed using a Solver P47 base and SMENA head. The preferred tip was a noncontact gold-coated NSG 11 (NT-MDT) with a force constant of 5 N/m and a resonant frequency of 190 kHz. All measurements were performed in the noncontact (tapping) mode at ambient conditions (25 °C in air).

**X-Ray Photoelectron Spectroscopy (XPS).** XPS spectra were measured on a VG Escalab 200 MK spectrometer equipped with an aluminum anode (Al  $K_{\alpha} = 1486.6$  eV) operating at 510 W with a background pressure of  $2 \times 10^{-9}$  mbar and a hemispherical analyzer connected to a five-channel detector. Measurements were carried out with 20 eV pass energy, 0.1 eV step, and 0.1 s dwelling time. Charging was typically around 0.5 eV. Energy correction was performed using the Si 2p peak of SiO<sub>2</sub> at 103.3 eV as a reference. The spectrometer was equipped with a transfer chamber (pressure  $5 \times 10^{-5}$  mbar) that allows the reduction of the samples under H<sub>2</sub> at elevated temperatures before the XPS analysis.

**Near-Edge X-ray Absorption Fine Structure (NEXAFS).** Soft X-ray absorption spectra (XAS) were collected at the undulator beam line U49/2-PGM1 of the third generation synchrotron radiation facility BESSY in Berlin, which operates with an electron energy of 1.7 GeV and a ring current below 250 mA. The Co L-edge with a spectral resolution of about 0.1 eV was recorded in a special apparatus previously described,<sup>16</sup> which allows "in situ" measurements to be performed at about 1–10 mbar depending on the gas phase. The NEXAFS signal was extracted from raw data by subtracting the preedge background using power series curves. Subsequently, the spectra were normalized by dividing by the height of the absorption edge at 802 eV.

Catalytic Activity. Selective hydrogenation of crotonaldehyde was carried out at atmospheric pressure in a mixture of 4 vol % crotonaldehyde (Aldrich >99+%) in hydrogen (Hoekloos, purity >99.99%). Typically, two pieces of model catalyst (ca. 2.5 cm<sup>2</sup> each one) were loaded in the reactor. The catalysts were reduced in flowing H<sub>2</sub> (60 mL/min) by heating at a rate of 5 °C/min to 450 °C and keeping the sample at this temperature for 1 h. The catalyst temperature was then adjusted to the desired reaction temperature. The catalytic measurements were performed both in flow and batch modes. The details of the batch mode measurements have been described elsewhere.<sup>17</sup> In short, the reactor was flushed with the reactant mixture for 5 min at the reaction temperature. The reaction was then carried out in batch mode by closing the reactor inlet and outlet. This was marked as zero reaction time. After a desired reaction time, a gas-phase sample was taken from the reactor using a precision sampling gas syringe that was injected into a GC-MS in order to analyze the reaction products: crotyl alcohol (CyOH), butanal (BA), and butanol (BOH). The next experiment was performed after the catalyst was treated under pure H<sub>2</sub> at the reaction temperature for 15 min. For both flow and batch measurements, the crotonaldehyde (CROTAL) conversion  $(X_{CROTAL})$  was



**Figure 1.** Typical RBS spectrum of Pt–Co bimetallic model catalysts. Inset: Pt and Co peaks for catalysts with different Pt/Co ratios.

 
 TABLE 1: Theoretical and Experimental Metal Loadings for Planar Model Catalysts

	theor load	etical ling <sup>a</sup>	experimental loading (RBS)			
	Pt	Со	Pt	Co	Pt/(Pt +	Co)
catalyst	(at/nm <sup>2</sup> )	(at/nm <sup>2</sup> )	(at/nm <sup>2</sup> )	(at/nm <sup>2</sup> )	theoretical	RBS
Pt	6	-	9	_	1	1
PtCo(1:1)	4.5	1.5	6.3	4.9	0.75	0.56
PtCo(1:2)	3	3	3.5	6.2	0.5	0.36
PtCo(1:4)	1.5	4.5	1.9	8.0	0.25	0.19
Co-10	—	10	—		0	
Co-6	-	6	-		0	

<sup>a</sup> Determined according eq 1 from refs 9 and 27.

calculated as  $X_{CROTAL}$  (%) =  $[\Sigma Yj/(\Sigma Yj + Y_{CROTAL})] \times 100$ , where  $\Sigma Yj$  is the sum of the molar fractions of the reaction products and  $Y_{CROTAL}$  is the unconverted molar fraction of crotonaldehyde. The selectivity to product *j* was determined as Sj (%) =  $[Yj/\Sigma Yj] \times 100$ . The conversion is expressed per 5 cm<sup>2</sup> of model catalyst, and these values were corrected for blank crotonaldehyde conversion measured using an empty reactor, which were typically lower than 1–2% of the catalytic activity measured on model catalysts. The hydrogenation activities are reported as moles of crotonaldehyde converted per (Pt + Co) atoms per second.

#### Results

A series of bimetallic Pt–Co/SiO<sub>2</sub> catalysts with varying Pt/ Co ratios was prepared by spin-coating as previously described. When  $[Pt(NH_3)_4](NO_3)_2$  and  $Co(NO_3)_2$  solutions were mixed, a  $Co(OH)_2$  precipitate was obtained. The precipitate was redissolved by the addition of NH<sub>3</sub> solution forming a Co ammine complex. For comparison purposes, Co and Pt monometallic catalysts were also prepared. Co and Pt loadings were determined by Rutherford Backscattering Spectrometry (RBS). Figure 1 displays the RBS spectra and the metal loadings are summarized in Table 1.

Theoretical loadings were computed using the following equation:<sup>9,27</sup>

$$m = 1.35 \times C_{\rm o} \sqrt{\frac{\eta}{\rho \omega^2 t_{\rm evap}}} \tag{1}$$

where *m* is the amount of material deposited onto the wafer,  $C_o$  is the concentration of precursor in the impregnating solution,  $\omega$  is the rotation speed,  $\eta$  and  $\rho$  are the viscosity and density of the impregnating solution (water), respectively, and  $t_{evap}$ , is the

evaporation time. In all cases, higher Co and Pt loadings were obtained than those predicted by eq 1, probably due to a stronger support-precursor interaction when ammine complexes are used. However, the spin-coating technique does allow the preparation of bimetallic catalysts with different metal ratios.

It is important to mention that both the Co and Pt peaks in the RBS spectra do not show any tail, indicating that relatively small particles were obtained. Furthermore, the analysis of the Si peak permits the estimation of the thickness of the SiO<sub>2</sub> layer. The thickness of the SiO<sub>2</sub> layer was found to be constant at around 20 nm. Hence, the SiO<sub>2</sub> layer is thick enough to be considered as a true SiO<sub>2</sub> phase.<sup>9</sup>

The unreduced model catalysts were characterized by AFM. The AFM images in Figure 2 indicates that for the preparations based on the ammine precursors no particles were observed, rather "flattish layer like structures" were obtained in all cases. For catalyst PtCo(1:2), although there seems to be some particle structure present, these have very low heights ( $\approx$ 1.5 nm). Most of the images taken for this catalyst showed a pattern similar to the images obtained for samples PtCo(1:1) and PtCo(1:4). In summary, the morphological characteristics of the catalysts seem to be similar and homogeneous.

**XPS Characterization.** The reduction of the bimetallic Pt– Co model catalysts was investigated by XPS. The calcined model catalysts were reduced under 1-1.5 mbar of hydrogen in the XPS prechamber and then transferred to the main chamber without any exposure to air.

Figure 3 shows the Co 2p spectra of samples PtCo(1:2) and PtCo(1:4) after reduction at different temperatures. The binding energies computed by standard peak fittings are summarized in Table 2. The Co 2p spectrum of the calcined catalysts show the characteristic pattern of oxidic cobalt, with the Co  $2p_{3/2}$  peak at 781.7–782.1 eV and a strong shake up feature at higher binding energy, in agreement with previous work.<sup>10</sup>

Figure 3 also shows that the reduction of Co starts at relatively low temperature. For sample PtCo(1:4), a significant fraction of cobalt is already reduced at 275 °C as clearly indicated by the Co  $2p_{3/2}$  peak at 778.3 eV.<sup>18</sup> As a reference, the Co 2p spectrum of cobalt foil obtained after a sputter cleaning has a Co  $2p_{3/2}$  binding energy of 778.2 eV. The fraction of cobalt that is fully reduced to Co<sup>0</sup> is very high in bimetallic catalysts reduced at 420 °C. Interestingly, the Co  $2p_{3/2}$  binding energy is slightly shifted to higher BE (0.2–0.3 eV) as the Pt/(Pt + Co) ratio increases.

Figure 4 shows the Pt 4f spectra of samples PtCo(1:2) and PtCo(1:4) after reduction at different temperatures, binding energies in Table 2. As a reference, the Pt  $4f_{7/2}$  binding energy corresponding to the Pt foil is 71.6 eV. Obviously, platinum is easily and fully reduced at low temperature. However, it is important to note that the Pt  $4f_{7/2}$  binding energy shifts to lower values as the reduction temperature increases and the Pt/(Pt + Co) ratio decreases. For instance, a shift of about 0.2–0.3 eV is observed for sample PtCo(1:4) reduced at 420 °C. These shifts might indicate the presence of an electronic perturbation of both metals. Hence, to get more insight into the electronic properties the bimetallic catalysts were investigated by in situ NEXAFS spectroscopy.

Formation of the Active Phase Monitored by In Situ NEXAFS. Figure 5a shows the spectra of different reference compounds reported in the literature<sup>19</sup> and the L<sub>3</sub> edge NEXAFS spectrum corresponding to  $Co_3O_4$  obtained in our experimental set up. Note that the photon energy of the reference spectra taken from ref 19 was shifted for better comparison with our data. The L<sub>3</sub> spectra corresponding to reference oxidic Co phases



Figure 2. Typical AFM height images of Pt-Co bimetallic model catalysts, along with corresponding profiles from a scan indicated with a white line on each image.



**Figure 3.** Co 2pXPS spectra of calcined  $Pt-Co/SiO_2$  model catalysts after reduction at different temperatures compared to that of Co foil reference.

 TABLE 2: XPS Binding Energies for Calcined and Reduced

 Model Catalysts and Reference Compounds

		treatment		
	XPS		Reduced	Reduced
catalyst	peak	Calcined	@ 275 °C	@ 420 °C
	Co 2p3/2	782.1 eV	778.5 eV (Co0)	_
PtCo(1:1)	-		782.1 eV	
	Pt 4f7/2	72.0 eV	71.5 eV	-
	Co 2p <sub>3/2</sub>	781.7 eV	778.5 eV (Co0)	778.5 eV (Co <sup>0</sup> )
PtCo(1:2)			781.3 eV	780.9 eV
	Pt 4f7/2	72.0 eV	71.6 eV	71.5 eV
	Co 2p <sub>3/2</sub>	781.7 eV	778.3 eV (Co <sup>0</sup> )	778.3 eV (Co <sup>0</sup> )
PtCo(1:4)			781.7 eV	781.3 eV
	Pt 4f <sub>7/2</sub>	72.0 eV	71.5 eV	71.3 eV
Pt foil	Pt 4f <sub>7/2</sub>		71.6 eV (sputtered)	
Co foil	Co 2p <sub>3/2</sub>		778.2 eV (sputtered)	

have been already discussed in the literature.<sup>19</sup> In short, the Co  $L_3$  edge of CoO and Co<sub>2</sub>SiO<sub>4</sub> are very similar because, in both cases, Co<sup>2+</sup> ions are octahedrally coordinated to oxygen.



**Figure 4.** Pt 4fXPS spectra of calcined  $Pt-Co/SiO_2$  model catalysts after reduction at different temperatures.

The spectrum of the Co foil after in situ sputtering and reduction under 1 mbar of hydrogen is also displayed in this figure. The metallic Co  $L_3$  spectrum is very similar to those reported in the literature.<sup>20</sup> The metallic  $L_{III}$  edge of transition metals consists mainly of an asymmetric absorption white line. This asymmetric peak can be described by the addition of two contributions: 1, a main peak corresponding to the  $L_3$  transition; and 2, a small contribution on the high-energy side which could be associated to a "shake up" feature in the XPS spectrum. Although some fine structure has been observed in the  $L_3$  edge of Ni<sup>21</sup> (which can be attributed to a critical point in the band structure), the  $L_3$  edges of Fe and Co seem to be featureless.

Figure 5b displays the Co L<sub>3</sub> edge corresponding to calcined Pt–Co model catalysts measured at room temperature under 0.5 mbar of H<sub>2</sub>. The spectrum of a monometallic catalyst (10 Co atoms/nm<sup>2</sup>) is also included in this figure. It is clear that this spectrum looks very similar to that of Co<sub>2</sub>SiO<sub>4</sub> or CoO, suggesting that cobalt is mainly forming octahedrally coordinated Co<sup>2+</sup> species. Clearly, the Co L<sub>3</sub> edge is significantly modified as the Pt/(Pt + Co) ratio increases. For instance, for



Figure 5. (a) Co L<sub>3</sub>-edge NEXAFS spectra of reference compounds. (b) Evolution of the Co L<sub>3</sub>-edge NEXAFS spectrum of calcined catalysts as a function of the Pt/ (Pt + Co) ratio.



Figure 6. Co  $L_3$ -edge NEXAFS spectrum of a calcined Co/SiO<sub>2</sub> catalyst, along with a weighted linear combination of NEXAFS spectra of Co<sub>2</sub>SiO<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>.

TABLE 3: Fittings of NEXAFS Spectra of Unreduced Catalysts Using a Linear Combination of Reference Compounds (Co<sup>0</sup>, Co<sub>2</sub>SiO<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>)

_			-		
catalyst	Pt/(Pt + Co)	Co <sup>0</sup> (%)	Co <sub>2</sub> SiO <sub>4</sub> (%)	Co <sub>3</sub> O <sub>4</sub> (%)	$R^2$
Co-10 PtCo(1:4) PtCo(1:1)	0 0.19 0.56	0 17 40	80 83 60	20 0 0	0.977 0.990 0.980

the catalyst with the highest Pt/(Pt + Co) ratio, sample PtCo-(1:1), the shape of the edge seems to indicate that the catalyst is partially reduced. To obtain a more quantitative description of the Co L<sub>3</sub> edge of the model catalysts, a simple linear combination of the reference compounds can be used. However, it is not sufficient to consider only the electronic state of the metal of interest to perform a linear combination analysis for nanometer scale clusters smaller than 2 nm.<sup>22</sup> Figure 6 shows that the Co L<sub>3</sub> edge of sample Co-10 is satisfactorily described by a weighted linear combination of Co2SiO4 and Co3O4 NEXAFS spectra. The contributions resulting from the best fit were 80% and 20%, respectively. In a similar manner, the spectra of the calcined bimetallic catalysts were fitted. Table 3 summarizes the fitting parameters. An increase of the reduction degree as the Pt(Pt + Co) ratio increased is clearly observed, probably due to a reduction induced-effect by the synchrotron beam. It is well-known that Pt reduces very easily. Then, hydrogen molecules could be activated on metallic Pt sites, partially reducing Co cations. This also suggests that both metals, Pt and Co, are in close interaction.



Figure 7. Evolution of Co  $L_3$ -edge NEXAFS spectrum of Pt–Co bimetallic catalysts reduced in situ under 0.5–1 mbar of  $H_2$  at various temperatures.



**Figure 8.** (a) Co  $L_3$ -edge NEXAFS spectrum of PtCo(1:1)/SiO<sub>2</sub> catalyst reduced at 300 °C, along with a weighted linear combination of NEXAFS spectra of reference compounds, showing that cobalt is already fully reduced to Co<sup>0</sup>. (b) Normalized Co  $L_3$ -edge NEXAFS spectrum of reduced Pt–Co/SiO<sub>2</sub> bimetallic catalysts as compared to those of reduced Co/SiO<sub>2</sub> catalyst and Co foil.

The samples were then reduced in situ under 0.5-1 mbar of H<sub>2</sub> at two different temperatures: 150 and 300 °C. Figure 7 shows the evolution of the Co L<sub>3</sub> edge as a function of the reduction temperature for samples PtCo(1:1) and PtCo(1:4). Cobalt seems to be fully reduced when the catalysts were treated under hydrogen at 300 °C, which is significantly lower than the temperature required to fully reduce cobalt during the XPS measurements discussed above. It is important, however, to note that the NEXAFS measurements were taken under H<sub>2</sub> and, as already mentioned, a reduction induced-effect by the synchrotron beam cannot be ruled out. As described before, the spectra of the bimetallic samples reduced at 300 °C have been analyzed using a linear combination of L<sub>3</sub> edge spectra of reference compounds. Figure 8a shows that the Co L<sub>3</sub> edge of sample PtCo(1:1) is satisfactorily described by using only the spectrum of Co foil. It is important to mention that the addition of a very small contribution of the L3 edge spectrum corresponding to a known Co oxide phase (CoO,  $Co_2SiO_4$  or  $Co_3O_4$ ) does not lead to a better description of the L<sub>3</sub> edge spectrum of sample PtCo-(1:1). However, the existence of a small fraction of an unknown Co oxide species such as a Co suboxide cannot be completely

TABLE 4: Ratio of the "White Line" Areas of  $L_{2,3}$  Edges Taking the Co Foil as a Reference

sample	$AWL_3^{j}/AWL_3^{foil}$	$AWL_2^j/AWL_2^{foil}$
Co foil	1	1
Co-6	1.30	1.15
PtCo(1:4)	1.50	1.24
PtCo(1:2)	—	—
PtCo(1:1)	1.74	1.50

ruled out. Similar results were also obtained for the other samples. Thus, our data indicate that cobalt is most likely fully reduced.

To obtain more insight on the electronic state of Co after reduction, the NEXAFS spectra of the reduced samples were analyzed in further detail. First, the preedge background was removed using a standard procedure. Then, the L<sub>2,3</sub> spectra were normalized dividing the absorption spectra by the height of the edge jump. The normalized L<sub>2,3</sub> spectra are presented in Figure 8b. For comparison, the spectrum of the Co foil is also displayed in the figure. It is clear that the intensity of the "white lines" increased as the Pt loading increases. To obtain a more quantitative analysis of the evolution of the white line intensity as a function of the Pt/(Pt + Co) ratio, the white line areas of both edges  $(AWL_i)$  were determined. Each edge can be roughly described as the sum of a sharp peak (WL) plus a step function.<sup>23</sup> After subtracting an arctangent function, the resulting curves were numerically integrated between 774 and 790 eV and between 790 and 802 eV for the L<sub>3</sub> and L<sub>2</sub> edges, respectively. Then, the  $AWL_i^{j/A}WL_i^{foil}$  ratios, where  $AWL_i^{j}$  is the white line area of sample j at the L<sub>i</sub> edge and AWL<sub>i</sub><sup>foil</sup> is the white line area of Co foil at the  $L_{i}$  edge, were computed. Table 4  $% \left( {{L_{i}}} \right)$ summarizes the values of these ratios. It was also found that the position of the maximum is slightly shifted to lower energy as Pt/(Pt + Co) ratio increases. Interesting, the  $AWL_i^{j}/AWL_i^{foil}$ ratios increase for both  $L_{2,3}$  edges as the Pt/(Pt + Co) ratio increases. Furthermore, the fractional charge transfer can be estimated according to the method developed by Mansour et al.<sup>24</sup> Thus, the fractional charge transfer is expressed as:

$$f_{\rm D} = (\Delta A_3 + 1.11 \Delta A_2) / (A_3 + 1.11 A_2)$$
(2)

where

$$\Delta A_{i} = (L_{i}area)_{alloy} - (L_{i}area)_{pure-metal}$$
(3)

The factor 1.11 is derived from the fact that the  $L_2$  XAS spectrum should be multiplied by 2.22 to obtain the area of the  $L_3$  XAS spectrum,<sup>24</sup> and not by 2 as expected since the degeneracy for the  $2p_{3/2}$  states is twice that for  $2p_{1/2}$  states. For cobalt, we have found an experimental ratio between the  $L_3$  and  $L_2$  areas (branching ratio) of about 3. It is known that the  $L_3/L_2$  ratio in the 3d transition metals deviates form the 2:1 theoretical ratio.<sup>25,26</sup> Leapman and Grunes<sup>23</sup> found  $L_3/L_2$  ratios of 3.3 and 3.4 for Ni and Fe, respectively. Therefore, we propose to use a factor of 1.5 instead of 1.11 in equation [2] to estimate the fractional charge transfer. Figure 9 shows the increase of both  $L_{2,3}$  edges as a function of the Pt/(Pt + Co) ratio. As a consequence, the fractional charge transfer also increases.

**Catalytic Testing.** Crotonaldehyde hydrogenation proceeds through a parallel-consecutive reaction pathway (Scheme 1), involving the hydrogenation of C=C and C=O double bonds. While a single hydrogenation step leads to the primary reaction product (butanal, the saturated aldehyde and crotyl alcohol, the unsaturated alcohol), a consecutive hydrogenation step produces butanol, the fully hydrogenated reaction products.



**Figure 9.** Evolution of the normalized "white line" areas of  $L_{2,3}$  edges and of the fractional charge transfer ( $f_D$ ) as a function of the Pt/(Pt + Co) ratio.

SCHEME 1: Reaction Network of Crotonaldehyde Hydrogenation



# n-Butyraldehyde

The catalytic measurements were carried out over a temperature range between 100 °C and 150 °C. Figure 10a shows the evolution of crotonaldehyde conversion at 100 °C normalized per 5 cm<sup>2</sup> of model catalyst as a function of reaction time, operating the reactor in batch mode. Only the bimetallic catalysts with higher Pt/(Pt + Co) ratios, PtCo(1:1) and PtCo(1:2), were included in the figure because of the activity of sample PtCo-(1:4) was almost zero under these reaction conditions, although it was catalytically active at higher temperatures. While Pt-Co catalysts exhibit a relatively good linear relationship between conversion and reaction time, the monometallic one significantly deviates from this behavior. This suggests that the addition of Co could play a role in decreasing deactivation by coke formation. Nevertheless, the initial slope is representative of the reaction rate when the reactor is operated in batch mode. It is therefore clear that the addition of Co, up to certain limit, leads to an increase of catalytic activity rather than a decrease, as is often observed for bimetallic systems. However, an optimum Pt/(Pt + Co) ratio clearly exists. It is important to mention that the catalytic measurements reported in Figure 10 were performed in batch mode and, therefore, coke deactivation might play an important role. Thus, the increase in the catalytic activity as the Pt/(Pt + Co) ratio increases, at least up to a Pt/ (Pt + Co) ratio of 0.36, might also be explained by a lower



**Figure 10.** Selective hydrogenation of crotonaldehyde on Pt–Co bimetallic model catalysts and on a Pt model catalyst (reaction in batch mode at 100 °C). (a) Crotonaldehyde conversion as a function of reaction time. (b) Selectivities toward crotyl alcohol and butanol as a function of reaction time.



**Figure 11.** Arrhenius plot for crotonaldehyde hydrogenation in flow mode on Pt–Co and Pt model catalysts.

coke deactivation in the bimetallic systems. More important than the promoting effect on the catalytic activity is the effect of Co addition on the selectivity pattern. Figure 10b also displays the evolution of the selectivities as a function of reaction time (for the sake of clarity, the selectivity toward butanal which remains nearly constant as a function of time was not included in this figure). As expected, the monometallic Pt sample exhibits an extremely low selectivity toward crotyl alcohol,  $S_{CyOH}$  (%)  $\approx$ 3%. Moreover, the selectivities are nearly constant as a function of time and even at higher reaction times the formation of *n*-butanol is rather low, clearly pointing out that Pt supported on SiO<sub>2</sub> is intrinsically unselective for hydrogenating this functional group.

To get more insight on the catalytic behavior in the crotonaldehyde hydrogenation, complementary measurements in flow mode were also carried out on selected samples: Pt and PtCo-(1:2). Figure 11 displays the Arrhenius plot for both samples. The apparent activation energies ( $E_{act}^{app}$ ) are 55.7  $\pm$  2.4 kJ/ mol and 46.7  $\pm$  2.3 kJ/mol, respectively. It is important to emphasize that while the monometallic catalyst produces almost exclusively *n*-butyraldehyde and an increasing amount of *n*-butanol at higher temperatures ( $S_{CyOH}$  (%)  $\leq$  3%), the bimetallic one is significantly more selective toward the



**Figure 12.** Evolution of the selectivity toward crotyl alcohol as a function of crotonaldehyde conversion, measured at various reaction temperatures (reaction in batch mode).



Figure 13. Selective hydrogenation of crotonaldehyde on planar model catalysts (reaction in batch mode). Catalytic activity and selectivity toward crotyl alcohol as a function of the Pt/(Pt + Co) ratio.

unsaturated alcohol ( $S_{CyOH}$  (%)  $\approx 10-15\%$ ) and no consecutive hydrogenation is observed ( $S_{BOH}$  (%)  $\approx 0\%$ ).

Figure 12, in line with the results discussed above, shows that the selectivity toward the unsaturated alcohol is decreased as reaction temperatures increases, when the reactor is operated in batch mode. As expected, the  $S_{CyOH}$  also decreases as the reaction time is increased, but mainly due to an increase of the selectivity of *n*-butanol, i.e., the fully hydrogenated compound, which is a secondary reaction product.

Figure 13 summarizes the catalytic behavior of Pt–Co bimetallic planar catalysts in selective hydrogenation of crotonaldehyde. This figure clearly shows that the addition of Co not only increases the selectivity toward the unsaturated alcohol significantly but also the intrinsic activity of Pt seems to be increased.

In short, the obtained results can be summarized as follows: - Pt–Coplanar model catalysts with various Pt/Co ratios have been successfully prepared by the spin-coating technique.

- Upon reduction at high temperature, the BE of Pt and Co were slightly shifted to lower and to higher values, respectively.

- NEXAFS shows that the cobalt is fully reduced to  $Co^0$  at relatively low temperature and the intensity of the "white lines" increased as the Pt loading increases.

- Pt–Co bimetallic catalysts exhibit an improved catalytic behavior in the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes.

## Discussion

The results reported in this contribution illustrate the feasibility of preparing and testing bimetallic planar model catalyst. A great advantage of this approach is that both the physicalchemical characterization and the catalytic testing are performed on the same particles, which is crucial to correlate unequivocally the structural/ electronic properties with the catalytic behavior. Furthermore, the kinetics is not perturbed by diffusion limitations.<sup>17</sup> Although the model catalyst approach has been extensively applied in catalyst research,<sup>9</sup> we stress here that to the best of our knowledge these are the first bimetallic model catalysts reported in the literature which have been prepared by a simple spin-coating technique. This technique allows for the preparation of a realistic industrial model because the catalytically active materials are applied via wet chemical impregnation procedure as used by industry.<sup>10</sup>

A large number of techniques, including RBS, AFM, XPS, and NEXAFS, were used to characterize the unreduced bimetallic catalysts. As already mentioned, higher Co and Pt loadings were obtained than those predicted by eq 1. This equation has been used to accurately predict metal loadings of model catalysts prepared by spin-coating technique.<sup>27</sup> It is important to mention that, in most cases, solutions of simple metallic salts such as nitrates or chlorides were used for impregnation, which are slightly acids. In the present study, we have used solutions of ammine complexes with a relatively strong basic pH of about 11. Obviously, a much stronger support-precursor interaction is expected in this case. As eq 1 was deduced from purely physical considerations, no chemistry is taken into account. Hence, this equation predicts accurate loading when the supportprecursor interactions are relatively weak while the experimental loadings could deviate to higher values when strong supportprecursor interactions exist.

For unreduced catalysts, the position of the XPS peak is shifted to higher binding energy as compared to the binding energies reported in the literature for  $CoO/Co_3O_4^{28-32}$  and  $Co-(OH)_2^{28,33}$  of around 780.4 and 780.9 eV, respectively. Recently, Backman et al.<sup>34</sup> reported a Co  $2p_{3/2}$  binding energy of 781.9 eV for Co<sub>2</sub>SiO<sub>4</sub> reference compound. We therefore take the higher Co  $2p_{3/2}$  binding energy as evidence formation of a Co<sub>2</sub>-SiO<sub>4</sub>-like interface structure. Furthermore, fits of the NEXAFS spectra using linear combinations of reference compounds were always better when Co<sub>2</sub>SiO<sub>4</sub> was used as a reference compound instead of CoO, also suggesting the formation of Co<sub>2</sub>SiO<sub>4</sub>.

**Reduced Catalysts.** When bimetallic Pt–Co catalysts were reduced a high temperature and depending on the Pt/(Pt + Co) ratio, the Co  $2p_{3/2}$  binding energy is slightly shifted to higher BE while the Pt  $4f_{7/2}$  binding energy shifts to lower values. Although the core-level shifts cannot be directly correlated with an electronic transfer between Pt and Co since the final states, i.e., screening of the core hole, may also play an important role,<sup>3</sup> these shifts might still indicate an electronic perturbation of both metals. The following reasons can be invoked to explain a corelevel shift: 1, particle size effect (smaller size, higher BE); 2, isolation or dilution (orbital rehybridization); 3, electronic transfer.

Since the catalysts were activated under mild conditions (*T* not higher than 450 °C), we do not expect significant differences in particle size as indicated by XPS (no changes in the XPS  $I_{Pt}$   $4t/I_{Si}$   $_{2p}$  ratio were observed as the reduction temperature increased from 275 to 420 °C). Moreover, a reduction in particle size should occur to explain the upward shift of Co 2p BE as the reduction temperature increases. On the other hand, a negative shift in the Pt  $4f_{7/2}$  BE as compared to that of the Pt foil was observed as the reduction temperature increased. This

cannot be explained by a particle size effect. Therefore, the XPS shifts are most likely due to an electronic modification of both Pt and Co.

NEXAFS data show that cobalt is fully reduced to  $Co^0$  and the intensity of the L<sub>2,3</sub> white lines is increased as the Pt loading increases. Normally, an increase or decrease of the intensity of the white line is attributed to an electronic modification of the absorbing atoms,<sup>35,36</sup> in our case the Co atoms.

The summation rule in XAS spectroscopy states that the integrated intensity for a given absorption edge reflects the total number of empty states with the proper symmetry.<sup>37</sup> The  $L_{2,3}$ edges of transition metals involve resonances (white lines) that are  $2p \rightarrow 3d$  transitions, along with much weaker  $2p \rightarrow 4s$  transitions ( $\approx$ 20-fold weaker), multielectron features, and 2p $\rightarrow$ continuum transitions<sup>36,38</sup>. We can expect a significant correlation between the number of d- holes in the metal band and the integrated areas. As compared to the Co foil, the intensity of both white lines is increased. However, it seems that the  $L_3$ edge is modified to a large extent as indicated by a higher increase of the WL as compared to that observed at the  $L_2$  edge. The  $L_3$  edge is significantly different from the  $L_2$  edge for 3d metals compounds. The origin of this fact is mainly due to the 3d spin-orbit coupling and the overlap between the 2p wave function and the d wave function, the multiplet effects,<sup>26,39</sup> which might be affected to a different extent in our Pt-Co bimetallic systems. Morrison et al.<sup>40</sup> reported a decrease of the branching ratio in  $Fe_XGe_{1-X}$  alloys.

Recently, Wang et al.<sup>41</sup> reported that the integrated intensity of L<sub>2,3</sub> edges of Ni complexes can be used to quantitatively determine the number of 3d vacancies. Whereas the L<sub>2,3</sub> edges of 5d metals have been frequently used to study electronic modifications of the d-band in catalysis research, the L<sub>2,3</sub> edges of transition metals have been used less. L edge intensities have also been used to quantify charge transfer in platinum–nickel single crystals,<sup>42</sup> platinum–cobalt alloys,<sup>43</sup> and iridium catalysts.<sup>44</sup> We can conclude, therefore, that the simultaneous increase of both L<sub>2,3</sub> white lines indicates that the unoccupied d<sub>5/2</sub> and d<sub>3/2</sub> densities of states (DOS) are increased.

The method developed by Mansour et al.<sup>24</sup> aims at determining the charge fractional change of the number of d-band vacancies relative to a reference material. Using this method we have found that the fractional charge transfer increases as the Pt/(Pt + Co) ratio is increased, which indicates a decrease in the electron density of Co, probably via electron transfer or rehybridization of the orbitals upon alloying.

The decrease of the electron density of Co shown by in situ NEXAFS spectroscopy is in line with the XPS measurements, which showed a shift in the XPS peaks for both Pt and Co XPS after reduction at high temperature. The existence of electronic modifications in Pt-based bimetallic catalysts has been frequently invoked in the literature.<sup>1-3</sup> In most of cases, the electronic modification was derived from XPS data. Zsoldos et al.45 reported the formation of Pt-Co alloys based on the 0.5 eV shift of Co 2p peak toward higher BE. More recently, the use of XAS allows one to get more insight into the nature of these electronic modifications. The analysis of the L<sub>2.3</sub> edges of 5d metals, in particular Pt, has been extensively used. Moraweck et al.<sup>42,46</sup> reported an electron transfer from nickel/ iron to platinum based on the variation in the number of holes in the Pt 5d band. In this contribution we clearly demonstrate the existence of electronic modifications in Pt-Co alloys by analyzing the  $L_{2,3}$  edges of Co. Such an approach has not been taken previously.

The apparent activation energies derived from an Arrhenius plot are significantly higher than the activation energies often reported in the literature for Pt-based catalysts,<sup>47–49</sup> ranging from 20 to 35 kJ/mol. Raab and Lercher,<sup>50,51</sup> reported apparent activation energies of about 45 kJ/mol for Pt–Ni/SiO<sub>2</sub> and values ranging from 29 to 54 kJ/mol for titania supported catalysts. It is important to stress that our catalytic measurements were performed under essentially diffusion-limitation-free conditions since pores are absent in the planar model catalysts.

Slightly lower apparent activation energies for Pt-Sn bimetallic systems as compared to those of Pt catalysts have already been reported for the selective hydrogenation of crotonaldehyde both in gas49 and liquid phase.52 This slight decrease in the apparent activation energy could be explained invoking an electronic effect, which is readily present in our planar model catalysts as was unambiguously demonstrated by in situ NEXAFS spectroscopy. It is, however, important to mention that the decrease in the apparent activation energy could also be attributed to the increase in selectivity toward crotyl alcohol, i.e., hydrogenation of C=O double bond, observed for bimetallic systems. Raab and Lercher<sup>51</sup> found that the apparent activation energy for Pt-Ni/TiO2 catalysts increased as the Ni amount was increased, whereas the selectivity toward crotyl alcohol decreased. Recently, activation energies of 20  $\pm$  1 kJ/ mol and  $28 \pm 3$  kJ/mol for crotyl alcohol and *n*-butyraldehyde formation, respectively, were reported for Pt/ZnO.48 It is important to mention that, for sample PtCo(1:2), the apparent activation energy for *n*-butyraldehyde formation is  $52.1 \pm 2.4$ kJ/mol. This value is rather close to the apparent activation energy determined on the monometallic sample, which is in line with the decrease in the apparent activation energy as the selectivity toward the unsaturated alcohol increases.

The increase of selectivity toward the unsaturated alcohol in bimetallic systems has been frequently attributed to an ensemble and/or electronic effect.<sup>3,5,53</sup> Also, the formation of mixed sites, where both components participate in the catalytic process, has been invoked to explain the promoting effect in bimetallic systems.<sup>54</sup> However, the promoting effect strongly depends on the chemical nature of the promoters and the mechanism of promotion is still not well understood. In some cases, the promoters are not fully reduced and the mixed-site can be described as Pt- $M^{x+}$ , where the promoting effect is due to a positively charged cation M<sup>x+</sup>, which activates the C=O double bond.<sup>5,53-55</sup> This promoting mechanism is similar to the wellknown SMSI state<sup>56</sup> and particularly suited to explain the effect of alkali cations, where these metal cations are thought to act as a surface lewis site which can activate the C=O group. A similar mechanism has been proposed to explain the promoting effect of Fe, Co, and Sn on Pt- and Ru-based catalysts.55,57,58 Obviously, this promoting mechanism requires a partial reduction of the second metal. Although the coexistence of Sn species with different oxidation degrees (Sn<sup>IV</sup>, Sn<sup>II</sup>, and Sn<sup>0</sup>) has been frequently found in tin-promoted catalysts,<sup>49,52</sup> the existence of a large fraction of cobalt in oxidic state has been less often observed.59 Our in situ NEXAFS measurements clearly demonstrated that cobalt is fully reduced in our planar model catalysts. On the basis of these results, it has been proposed that Pt and Co form alloyed bimetallic particles, in which the electron density of cobalt is decreased due to electron transfer or rehybridization. Therefore, the beneficial effect of Co is related to an alloying effect. In these bimetallic Pt-Co clusters, cobalt exhibits a lower electron density as compared to that in Co monometallic clusters, activating the C=O double bond and, therefore, enhancing the selectivity toward the unsaturated

alcohol. We stress here that most of the studies reported in the literature on selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes on bimetallic systems were performed on high-surface area catalysts, which are often poorly characterized and sufficiently complex to establish unequivocal structure-catalytic activity relationships. Our approach using planar model catalyst allows us to gain more insight into the relationship between structural/electronic properties and catalytic behavior.

#### Conclusions

In this contribution we have demonstrated that bimetallic planar model catalysts can be successfully prepared by the spincoating techniques, which mimics the conventional impregnation technique used for industrial catalysts.

In situ NEXAFS measurements indicate that the unoccupied d density of states (DOS) of cobalt is increased upon alloying, probably due to electron transfer or rehybridization of the orbitals. NEXAFS is, therefore, a key technique to unravel structural/electronic properties of metallic/bimetallic clusters. We emphasize that this is a pioneering work in using the  $L_{2,3}$  edges of 3d transition metals to elucidate their electronic state in bimetallic clusters.

Selective hydrogenation of crotonaldehydes can be successfully performed on bimetallic planar model catalysts. The addition of Co promotes the C=O hydrogenation, increasing the selectivity toward unsaturated alcohol (Crotyl Alcohol). Selective hydrogenation of crotonaldehyde requires the use of promoted Pt catalysts since promoters are indispensable to activate the C=O group. We found that the activation mechanism of the C=O group in Pt-Co model catalysts involves the formation of Pt-Co alloyed clusters. The existence of Pt<sup> $\delta$ </sup>-Co<sup> $\delta$ +</sup> clusters is crucial to the adsorption of crotonaldehyde via the C=O group, favoring its activation. This is required to efficiently catalyze the hydrogenation of the C=O bond, producing crotyl alcohol selectively. This work demonstrates that planar surface science models can become an important tool to establish structure-activity relationships.

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