

CO Oxidation Activity and XPS Studies of Pt-Cu/ γ -Al₂O₃ Bimetallic Catalysts

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The kinetics and activity for CO oxidation of sintered and unsintered Pt-Cu/ γ -Al₂O₃ catalysts were studied. Hydrogen chemisorption, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) were employed to characterize the catalysts and interpret differences in catalytic activity. The results suggest that both separate and combined Pt-Cu entities coexisted in these catalysts. Preferential Cu enrichment was also observed in the combined entities. The activity of the sintered bimetallic catalysts increased slightly whereas the activity of the sintered Pt catalyst decreased significantly.

INTRODUCTION

Bimetallic catalysts have been developed and intensively studied in recent years (1-3). Most of the work on bimetallic catalysts has been devoted to hydrocarbon reactions relevant to petroleum refining (4, 5). Little is known about the activity of polymetallic catalysts in oxidation reactions such as CO oxidation, which is relevant in automobile exhaust pollution control. The objective of this work is to study this reaction in an attempt to gain some understanding of the nature of bimetallic systems during oxidation reactions. To this end, the studies presented here involve CO oxidation and activity measurements over Pt-Cu/ γ -Al₂O₃ catalysts in the unsintered and sintered states. Catalysts characterization was carried out by H₂ chemisorption, XPS, and TEM.

Characterization of supported bimetallic catalysts is a difficult task due to interaction of the two metallic components. Various spectroscopic techniques and selective chemisorption of gases have been applied for such purposes. Delgass *et al.* (6) used XPS and SIMS to characterize Fe-Ru catalysts and found strong Fe enrichment of the bimetallic clusters. Sinfelt *et al.* (7) used

high-resolution electron microscopy to determine the morphology of Ru-Cu clusters and found that they possessed raft-like shapes. In subsequent studies by the same authors (8), bimetallic formation on a Pt-Ir catalyst was inferred from X-ray diffraction lines lying at positions midway between the corresponding lines for Pt and Ir metals. The problem of segregation or surface enrichment, well known in bulk metals alloys, can also occur in highly dispersed microclusters. Burton *et al.* (9) suggested that in these systems, surface enrichment of one component is expected to occur preferentially on edges and kinks where atoms with low coordination number exist. In this work, we use various characterization techniques in an attempt to gain some understanding of the nature of Pt-Cu/ γ -Al₂O₃ catalysts during CO oxidation.

EXPERIMENTAL METHODS

Catalyst. The platinum-copper catalysts employed in this work were prepared in our laboratory by coimpregnation of γ -alumina with salt solutions of Pt and Cu. Ten grams of γ -alumina (Harshaw Chemical, 200 mesh powder, 192 M²/g BET) was added to an aqueous solution of chloroplatinic acid and copper nitrate at the concentration required

to obtain the desired Pt/Cu ratio. The catalyst was then dried for 16 hr at 110°C and stored. To investigate the effects of sintering on catalytic activity, some catalysts were subjected to an additional heat treatment at 700°C in oxygen flow for 10 hr. Bimetallic catalysts containing 0, 8, 25, 40, 60, 75, and 100 wt% Cu of a total metal content (Pt + Cu) of 1% by weight were prepared. Table 1 provides a listing of catalysts composition in terms of both weight and atomic %, as well as manufacturer-supplied data on the γ -alumina itself.

Apparatus. The experimental unit consists of an integrated-reactor-chemisorption apparatus designed for reaction kinetic studies and *in situ* measurement of gas chemisorption by the pulse technique. A detailed description of the apparatus and the technique of hydrogen chemisorption have been presented elsewhere (10), consequently only a brief description will be presented in this paper.

The reactor consists of a quartz tube heated externally by an electrical furnace, controlled by a proportional temperature controller. The temperature is measured by a thermocouple imbedded in the catalyst

bed. Inlet and outlet reactant concentrations are measured by a gas chromatograph equipped with a 6-ft-long Porapak Q column. Gases are metered by fine control valves, measured by calibrated flowmeters, and fed into a manifold where they are mixed. One gram of fresh catalyst powder (200 mesh) was placed in the reactor and dried in Argon for 6 hr at 110°C followed by a reduction in H₂ for 12 hr at 500°C. Prior to each kinetic run, the catalyst was subjected to a standard pretreatment consisting of: (a) oxygen flow (70 cm³/min) for 2 hr at 360°C to remove carbon surface residues and (b) reduction in hydrogen flow (70 cm³/min) for 3 hr at 500°C. During reaction rate measurements, the reactor was operated isothermally as differential reactor using a total flow rate of 100 cm³/min and a variable CO inlet concentration up to 5 vol%. Another activity measurement denoted as light-off temperatures (LOT) consisted in runs at constant CO concentration (2 or 5%) while increasing the temperature from 70°C until total conversion was attained. The reactant mixture, in both LOT and kinetic experiments, consisted of CO, 20% excess oxygen over CO, and helium.

When the reactor is used as a chemisorption apparatus, ultra-high purity argon is sent first to an oxytrap (Alltech Associates) to remove traces of O₂, then to the catalyst bed and a thermal conductivity (TC) cell. Pulses of hydrogen diluted in argon are injected into the carrier stream by means of a sampling valve. The hydrogen pulses are adsorbed by the catalyst until saturation occurs, as detected by a T. C. cell. Prior to each chemisorption experiment, the catalyst was reduced in H₂ for 3 hr at 500°C followed by degassing in flowing argon for 6 hr (11). All chemisorption experiments reported here were carried out at 25°C.

The XPS spectra were recorded on a Hewlett-Packard (HP) 5950B ESCA spectrometer using monochromatic AlK α X-rays ($h\nu = 1486.6$ eV). The reduced samples were pressed into 7-mm-diameter by 1-mm-thick pellets which were mounted on

TABLE 1
Catalysts Properties

	γ -Alumina properties
Powder size (mesh)	200
BET area (m ² /g)	192
Total pore volume (cm ³ /g)	1.079
Range of pore radii (Å)	60 ~ 7600
Powder density (g/cm ³)	1.22
Impurities (wt%)	<0.02
Weight % (1% = 100)	Atomic % Cu
100 Cu	100
75Cu 25Pt	90.2
60Cu 40Pt	82.2
40Cu 60Pt	67.2
25Cu 75Pt	50.6
8Cu 92Pt	21.1
100 Pt	0

HP gold-plated sample holders. Sample preparation as well as the introduction into the spectrometer were performed under dry N₂ atmosphere. Some samples were also reduced *in situ* (H₂ flow, 500°C, 3 hr) in a pretreatment chamber attached to the spectrometer via a vacuum transfer system. Some samples were exposed to air prior to analysis but no significant differences in the photoemission spectra could be observed. A HP electron flood gun was used to minimize sample charging. All electron binding energies were referenced against the ubiquitous C 1s signal at 284.6 eV as suggested by Wagner *et al.* (12) or the Al 2p signal at 74.0 eV which is a characteristic value for γ -Al₂O₃ (13). Both reference signals agreed within 0.2 eV.

RESULTS

Surface Analysis by XPS

The photoemission spectra of Cu 2p, Pt 4d, Al 2p, O 1s, and C 1s were recorded. The more intense Pt 4f line could not be used because of an overlap with the Al 2p line. Quantitative analysis of the relative Cu and Pt surface atom fraction was done using the Pt 4d_{5/2} and Cu 2p_{3/2} lines. A linear background was subtracted from the peaks to discount the inelastically scattered electrons. The peak areas were obtained by computer integration and were corrected for instrumental parameters, photoionization cross-sections (14), and for differences in electron escape depth (15). With these normalizations, $I_{\text{Cu}}/(I_{\text{Cu}} + I_{\text{Pt}})$ is the atom fraction of Cu in the surface region if one assumes the presence of homogeneous, bimetallic Pt-Cu clusters. In Fig. 1 we plotted this ratio versus the Cu bulk atomic % and found Cu enriched surfaces. The straight line would be obtained in the absence of any surface enrichment phenomena. The error of our measurements is large simply because of the low concentrations of Pt and Cu which were close to the detection limit of the XPS technique generally considered at approximately 0.05 atom %.

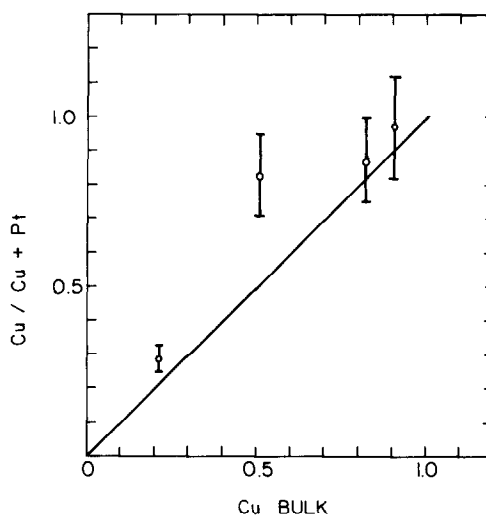


FIG. 1. XPS Cu intensity relative to Pt + Cu intensity versus Cu atomic bulk composition.

spite long counting times, spectra with poor signal-to-noise ratio were the results. However, our analysis was reproducible within the error limits indicated in Fig. 1.

The Cu 2p_{3/2} electron binding energy was found at 932.2 ± 0.1 eV typical for metallic Cu and Cu₂O (16). The structure of the Cu L₃M₄₅M₄₅ Auger line clearly indicated the presence of metallic Cu (17, 18). The lack of any shake-up satellite structure in the Cu 2p spectra pointed to the absence of any CuO or other Cu(II) compounds.

The Pt 4d_{5/2} photoelectron spectra were very broad (FWHM ≥ 4 eV) with their maximum intensity at about 313.4 eV. Reference values in literature are not available since all XPS work is done using the Pt 4f orbital. Therefore, we recorded the Pt 4d_{5/2} line of Pt black and found its position at 313.6 eV. Since a positive shift of more than 3 eV has been observed in the Pt 4f levels between metallic Pt and its oxides, a similar shift is expected for the 4d orbitals. Thus metallic Pt is the most likely species present on the catalyst surface.

Hydrogen Chemisorption

Table 2 lists the hydrogen uptake and platinum surface area results for six Pt-Cu

TABLE 2
Hydrogen Chemisorption Measurements on Pt-Cu/ γ -Al₂O₃ Catalysts

Composition		Catalyst condition	cm ³ H ₂ STP/g cat	V _{as} cm ³ H ₂ STP/g of Pt
wt% (1% = 100)	Atomic % Cu			
100 Cu	100.0	Unsintered	0.	0.
75Cu 25Pt	90.2	Unsintered	0.0406	16.24
60Cu 40Pt	82.2	Unsintered	0.0985	24.6
40Cu 60Pt	67.2	Unsintered	0.271	45.15
25Cu 75Pt	50.6	Unsintered	0.3545	47.27
100 Pt	0.	Unsintered	0.588	58.8
75Cu 25Pt	90.2	Sintered	0.006	2.41
25Cu 75Pt	50.6	Sintered	0.0974	13.0
100 Pt	0.	Sintered	0.104	10.4

catalysts. The amount of hydrogen uptake decreases with increasing Cu content. Figure 2 shows *specific hydrogen uptake*, i.e. (ml H₂ STP/g of Pt) versus atomic percent of Cu for these six bimetallic catalysts. The specific uptake accounts for the decrease in the Pt atoms as the amount of Cu increases. Hence if Pt and Cu particles were predominantly separate noninteracting entities, then at constant dispersion, the specific hydrogen uptake would be a horizontal line ex-

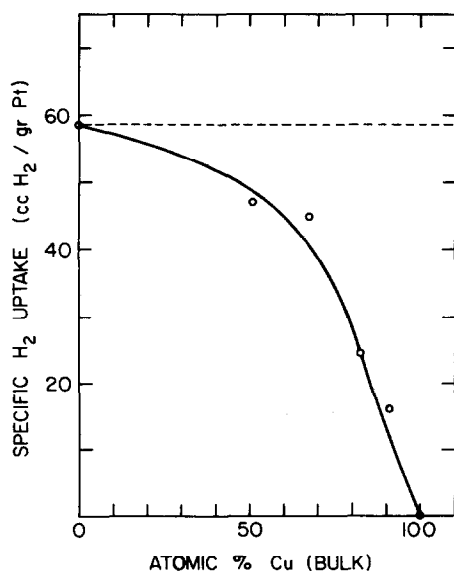


FIG. 2. Hydrogen uptake per gram of Pt versus Cu bulk composition.

cluding the 100% Cu sample. The data show that the specific hydrogen uptake decreases as Cu was added to the catalyst.

The decrease in H₂ uptake can be due to preferential Cu surface enrichment or to a decrease in Pt dispersion or both. To estimate possible relative changes in crystallite size distribution with Cu content, we used dark field transmission electron microscopy (TEM). Figure 3 shows electron micrographs of monometallic Pt and the 75Cu 25Pt catalyst. At the magnification used ($\times 130,000$) the highly dispersed material could not be resolved in this micrograph ($< 15\text{\AA}$). However, it seems that, above these sizes, there are no major changes in size distribution with increasing Cu content. Similar results were obtained with other bimetallic catalysts.

Kinetics and Activity

Kinetic experiments were carried out using a reactant mixture of CO, oxygen, and helium. The oxygen concentration was kept in excess over CO at about 20% by volume. Reaction rate vs CO concentration measurements were carried out isothermally at 106°C with CO concentrations varying from 0 to 5% by volume. Light-off temperature (LOT) experiments were also conducted at two CO concentrations, 5 and 2% by volume; the selected CO concentration was



FIG. 3. Transmission electron micrographs of (a) 100 Pt/ γ -Al₂O₃, and (b) 75 Cu 25 Pt/ γ -Al₂O₃ catalysts ($\times 130,000$).

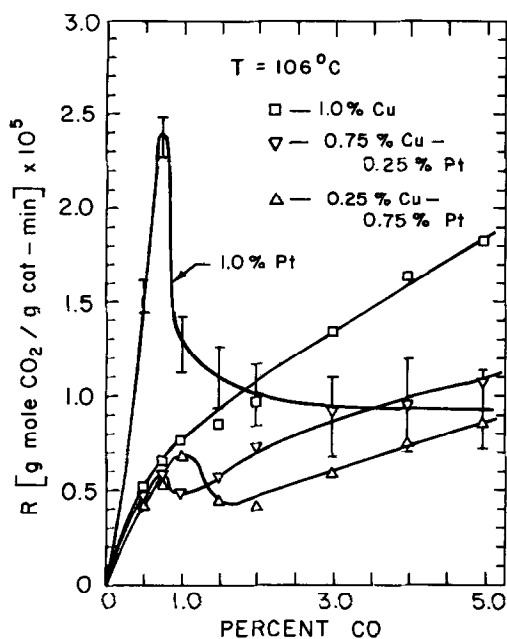


Fig. 4. Reaction rate versus CO concentration for four unsintered catalysts.

kept constant while increasing the temperature from 70°C to that of total conversion.

Figure 4 reveals the reaction rate (g mole CO₂/g cat-min) versus CO concentration for catalysts of different Pt-Cu composition. The reaction rate of a monometallic Pt catalyst exhibits the well-known kinetic behavior (19) in which the rate increases at low CO concentration, reaches a maximum and then decreases as CO concentration increases from about 1 to 5% by volume. For the Pt/ γ -Al₂O₃ catalyst, fluctuations of reaction rates were observed due to the fact that platinum catalyst exhibits oscillatory behavior (19). An infrared analyzer (Beckman 865), which could continuously monitor the CO₂ concentration of the product stream coming out of the reactor, allowed observation of the oscillatory phenomena that could not be continuously observed by gas chromatography. This self-sustained oscillatory phenomena is analyzed elsewhere (20).

For monometallic Cu, the reaction rate increases monotonically with CO concen-

tration as is characteristic of base metal catalysts (21). The rate curves for monometallic Pt and Cu cross at about 1.5% CO concentration, at which point the Cu catalyst is more active than the Pt catalyst since the latter is operating in the kinetic region where CO inhibition is manifest. The rate curves of the bimetallic catalysts follow the trend of the noble catalysts at low CO concentration, passing through what appears to be a local maxima. As CO concentration increases, the base metal function prevails and the rate increases monotonically. At high CO concentration, the 75Cu and 25Pt catalyst is as active as the Pt catalyst but less than monometallic Cu catalyst.

Figure 5 shows conversion versus temperature curves (LOT) of four different catalysts obtained at 5% CO except for the curve in broken line obtained at 2% CO. In comparing rate and LOT results, it is necessary to account for the differences in operating conditions used in both experiments. Rate results were obtained at low temperature (106°C) and variable CO concentration, whereas LOT were obtained at one concentration and variable temperature. Thus, only one point of the LOT curve (~106°C) is comparable with one point of the rate curves (2 or 5% CO). With this consideration in mind, the results in Figs. 4 and 5 are consistent. At 5% CO, the Pt catalyst is less active at low temperature than Cu and Pt-Cu catalysts, but as temperature increases the Pt catalysts gives higher conversion than all other catalysts. The 25Cu 75Pt catalyst exhibits a LOT which follows a trend similar to the Pt catalyst, but it is less active. Monometallic Cu does not exhibit a sharp LOT, which is characteristic of base metal catalysts with first order kinetics. The LOT of monometallic Pt obtained at 2% CO gives the highest conversion as expected from the rate data.

The effect of sintering, by exposure to pure oxygen for 10 hr at 700°C, was also investigated. Table 2 shows that hydrogen uptake was substantially reduced after sintering. Figure 6 shows the low temperature

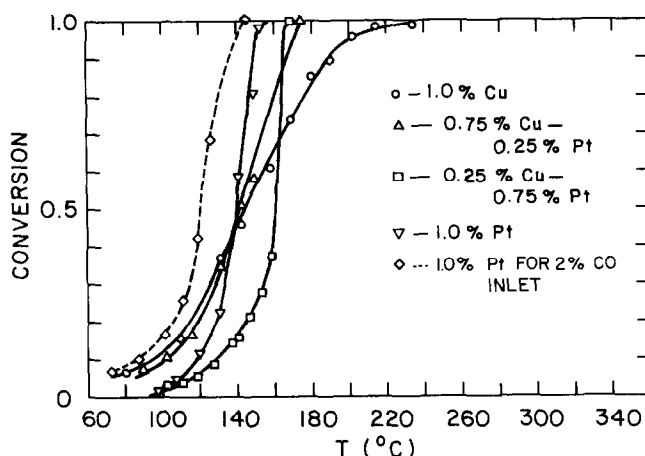


FIG. 5. LOT curves for four unsintered catalysts at 5% CO inlet concentration. Broken line curve is for 1% Pt/ γ -Al₂O₃ at 2% CO concentration.

rate data for the sintered catalysts. As expected, sintering reduces drastically the activity of the Pt catalyst, yet the bimetallic catalysts exhibit a slightly higher activity

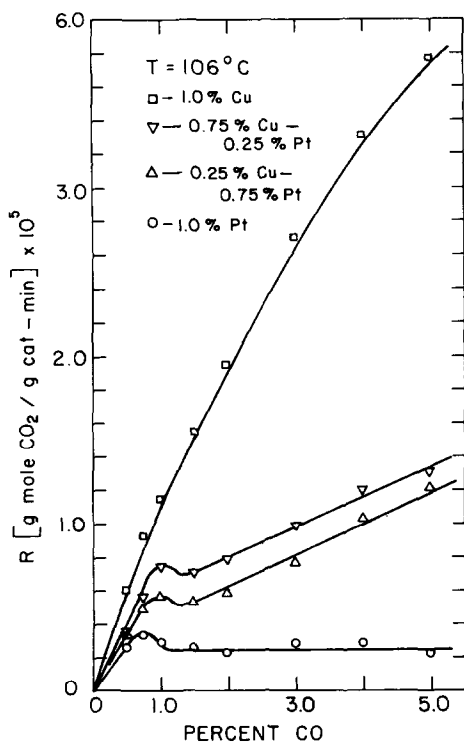


FIG. 6. Reaction rate versus CO concentration for four sintered catalysts.

than in unsintered form. The rate of the sintered Cu catalyst is higher than unsintered, particularly at high CO concentrations. Fig. 7 shows the LOT of monometallic Pt and Cu in both sintered and unsintered form. The activity loss of the Pt catalyst is evident by a significant shift of the LOT curves to higher temperatures. The LOT of sintered Cu is higher than the unsintered form only at low temperatures, consistent with the rate data (Fig. 6). At higher temperatures the situation reverses but the LOT of the sintered Cu catalyst is still higher than sintered Pt except near complete conversion. Dark field electron

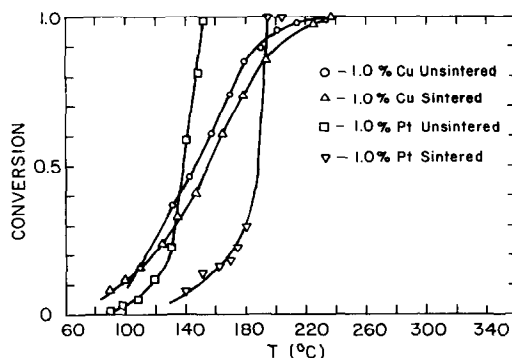


FIG. 7. LOT curves for sintered and unsintered 1% Pt/ γ -Al₂O₃ and 1% Cu/ γ -Al₂O₃ catalysts (5% CO concentration).

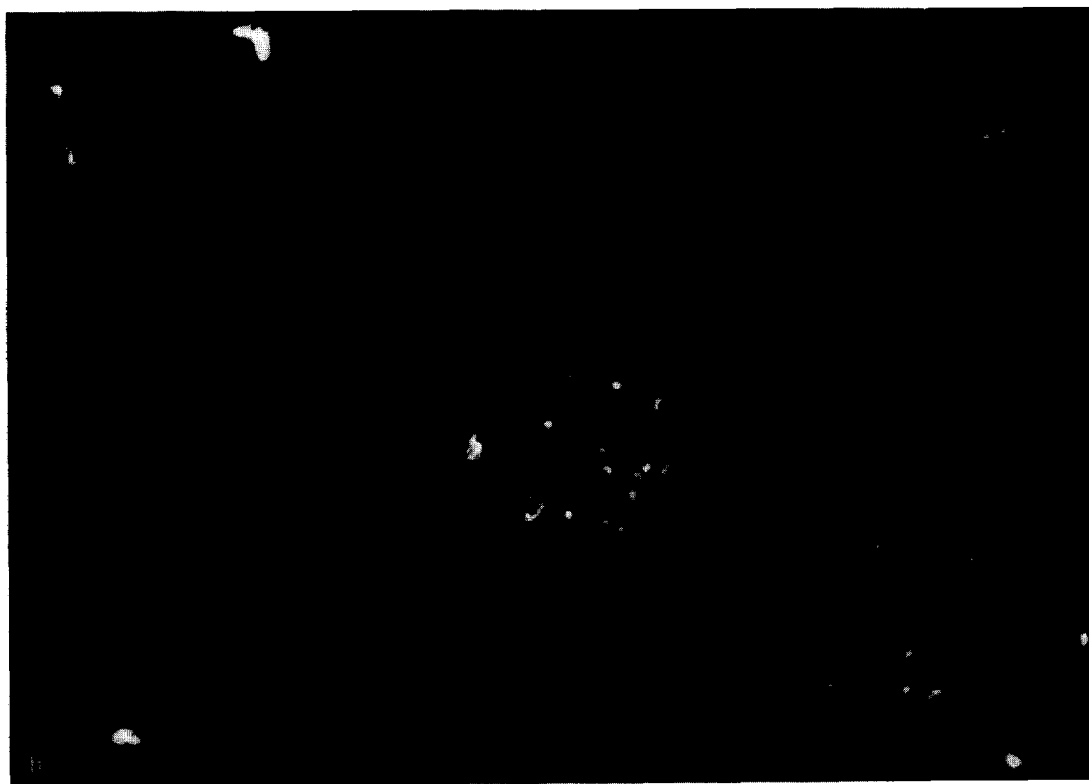


FIG. 8. Transmission electron micrographs of unsintered (a) and sintered (b) 75 Cu 25 Pt/ γ -Al₂O₃ sintered catalysts ($\times 130,000$).

micrographs of sintered and unsintered 75Cu 25Pt catalysts (Fig. 8) do not indicate that significant changes in crystallite size occurs.

DISCUSSION

XPS results suggest that Pt and Cu are present in metallic states since no detectable shifts in binding energies from Cu and Pt peaks were observed. Furthermore, Cu XPS relative intensity indicate that preferential Cu enrichment occurs in the surface region within the escape depth of photoelectrons. H₂ chemisorption results also indicate that Cu interferes with Pt decreasing specific hydrogen uptake.

If Cu and Pt exist as separate noninteracting entities, then at constant dispersion, Fig. 2 should be an horizontal line, excepting monometallic Cu. On the other hand, if we use Sinfelt's (7, 8) argument, a substantial decrease in H₂ uptake will result with addition of a few atom percent Cu signaling formation of alloy clusters with Cu surface enrichment. Figure 2 shows that neither one of the above situations predominates, which suggests the existence of both: separate and combined Pt-Cu entities. The detailed structure of this entity cannot be determined with the techniques used in this work. Electron diffraction patterns obtained during TEM measurements could not be used to determine bimetallic alloy formation since Pt and Cu render almost identical patterns. Furthermore, in the light of XPS and activity results, we speculate that the combined entities exhibit preferential surface Cu enrichment. This has been documented in the literature for Pt-Cu bulk alloys (21, 27). Surface enrichment for the Pt-Cu system is also predicted by several surface segregation models (23, 24). Whereas results obtained with bulk alloys are not directly applicable to highly dispersed systems, the concurrence of results is supportive of our interpretation.

The kinetic and LOT results also provide support that both separate Pt and Cu and combined Pt-Cu entities are present in our

catalysts. The bimetallic catalysts do not exhibit predominance of either the bimolecular Langmuir kinetics characteristic of Pt catalyst or the first-order kinetic characteristic of base metals. Instead, a mixed mode kinetic behavior with Pt-like behavior at low CO concentration, and Cu-like behavior at high CO concentration, characterize the bimetallic catalysts rate curves.

The increase in rate of the sintered bimetallic and Cu catalysts is in sharp contrast with the decrease in activity of the Pt catalyst. H₂ chemisorption indicates that the latter catalyst undergoes crystallite growth. Since Cu does not chemisorb H₂, it is difficult to ascertain the reason for activity increase of the Cu catalyst. The sintered catalysts were subsequently reduced in H₂ at 500°C prior to reaction, which might cause redispersion. Redispersion of Cu/Al₂O₃ catalysts after aging in oxygen and reduction in CO have been reported by several authors (25-29). The XPS relative intensities were 0.6 and 0.3 for the Cu catalyst in sintered and unsintered form which suggests that redispersion plays a role in the observed activity increase. In the case of sintered bimetallic catalysts, the XPS Cu relative intensity did not change significantly from that of the unsintered form. Thus, it is not possible to ascertain uniquely whether the activity increase in the sintered bimetallic catalysts was due to Cu redispersion or Pt-Cu interactions which modifies the sintering process.

In summary, the results suggest that on Pt-Cu/ γ -Al₂O₃ catalysts, both separate Pt and Cu and combined Pt-Cu entities coexist. Preferential Cu surface enrichment also appears to prevail in the combined entities.

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