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Determination of Metal Dispersion and Surface Composition in Supported Cu–Pt Catalysts

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A combination of adsorption and surface reaction probes has been used to characterize SiO_2-supported Cu–Pt catalysts. CO chemisorption at 300 K on the reduced catalyst measured only surface Pt atoms (Pt_s). Dissociative N_2O adsorption at 363 K produced a monolayer of oxygen on the Pt_s atoms and converted the Cu surface atoms (Cu_s) to a surface "Cu_2O" phase. The hydrogen titration reaction on this O-covered surface at 210 K occurred only with oxygen chemisorbed on Pt_s sites with no H spillover to the Cu_2O surface, thus providing a second measure of Pt_s atoms. In contrast, this titration reaction at 300 K provided evidence for H interaction with this Cu_s–O–Cu_s phase via a spillover process. CO adsorption on this O-covered surface created by N_2O dissociation resulted in CO adsorption on the Cu^{+1} sites and titration of the chemisorbed oxygen on the Pt_s atoms according to the two equations

$$Cu_s^{+1} + CO_{(g)} \rightarrow Cu_s^{+1}\text{–}CO,$$
$$Pt_s\text{–}O + 2CO_{(g)} \rightarrow Pt_s\text{–}CO + CO_{2\,(g)}.$$

Thus the total number of surface metal atoms ($Cu_s + Pt_s$) can be measured if there is no CO_2 adsorption. The difference between this number and that for Pt_s atoms gives the number of Cu_s atoms. The oxygen uptakes via N_2O dissociation as well as the net weight changes during the CO titration reaction predicted by these surface compositions were in agreement with values measured gravimetrically and with information deduced from X-ray diffraction measurements. DRIFT spectra of the reduced bimetallic catalyst showed only one band at 2061 cm^{-1} for CO on reduced Pt_s atoms, whereas CO adsorbed at 300 K after exposure of this catalyst to N_2O again produced this band plus another near 2125 cm^{-1}, with the latter band indicative of CO adsorbed on Cu^{+1} sites. No evidence for residual oxidized Pt_s atoms was observed, in agreement with the latter equation above.

INTRODUCTION

Bimetallic catalysts dispersed on refractory materials have been intensively investigated to determine and understand their catalytic activity and selectivity in selected chemical reactions. There is a special relevance to reactions occurring in petroleum refining to produce aromatic hydrocarbons, which are catalyzed by a Group VIII metal combined with another metal, such as Cu, Ag, Au, Mo, Re, Sn, Ce, or Cr (1–5), although the combination of two Group VIII metals has also been of interest (6–9). Supported Cu/group VIII bimetallic systems, including Cu–Pt (3, 10–13), Cu–Pd (10, 14–21), Cu–Ru (1, 2, 10, 22–27), Cu–Rh (28–30), and Cu–Ni (31, 32), have been used in reforming, hydrogenation, oxidation, and hydrodechlorination reactions. In such studies, information about metal dispersion and surface composition in the bimetallic catalyst is essential to gain knowledge about the catalytic role of each component in these reactions. Surface compositions of supported Cu-based bimetallic systems have been calculated based on hydrogen and carbon monoxide chemisorption and the assumption that irreversible adsorption did not occur on metallic Cu surface atoms, Cu_s^0, (3, 10, 11, 31, 32); however this assumption may be questionable because hydrogen chemisorption on supported metallic Cu particles has been measured, even near room temperature (15, 22), and the presence of the Group VIII metal could facilitate such adsorption. Consequently, new approaches to measure surface Cu atoms as well as the noble metal atoms are desirable so that overall metal dispersions and surface compositions can be determined.

Although it is complicated to determine quantitative surface compositions using conventional chemisorption methods, it is also difficult to acquire such information using spectroscopic techniques such as XPS, AES, and EDAX because the sampling depth includes more than the external monolayer of surface atoms (33). Infrared spectroscopy can be an efficient surface probe but seldom yields quantitative surface compositions. Thus, adsorption methods remain as the most sensitive and selective means to quantitatively probe bimetallic surfaces, and the challenge is to find appropriate adsorption probe gases coupled with temperature regions that allow one to differentiate between the two type of metal atoms present. Pt–Cu is a representative Group VIII–Group IB bimetallic system that has been investigated

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previously (3, 10–13), and an approach which could determine its metal dispersion and surface composition may also have applications to other dispersed Group VIII–Group IB metal combinations. It is acknowledged in these bimetallic catalysts that compositions, both surface and bulk, can vary from particle to particle, and some monometallic crystallites could exist. Consequently, the results for Pt and Cu, which have a broad miscibility range, reflect only the average properties exhibited.

We have recently studied N_2O adsorption on Pt at conditions under which an oxygen monolayer with a nominal stoichiometry of Cu_2O is established on metallic copper surfaces, i.e., 363 K and 0.1 atm, and it was found that the O monolayer coverage on Pt was very similar to that obtained during O_2 adsorption at 300 K. This O monolayer could be completely titrated by either H_2 or CO at 300 K according to the following reactions (34, 35), where the subscript s represent a surface atom:

$$\mathrm{Pt_s + N_2O_{(g)} \rightarrow Pt_s\text{–}O + N_{2(g)}}, \qquad [1]$$

$$\mathrm{Pt_s\text{–}O + 3/2H_2 \rightarrow Pt_s\text{–}H + H_2O_{(ad)}}, \qquad [2]$$

$$\mathrm{Pt_s\text{–}O + 2CO_{(g)} \rightarrow Pt_s\text{–}CO + CO_{2(g)}}. \qquad [3]$$

On the Cu_s–O–Cu_s surface (designated "Cu_2O") established during dissociative N_2O adsorption (36–40), there is no irreversible H_2 adsorption at 300 K but irreversible CO chemisorption does occur as shown below (36, 41, 42):

$$\mathrm{Cu_s^{+1} + CO \rightarrow Cu_s^{+1}\text{–}CO} \qquad [4]$$

In addition, there is no irreversible CO adsorption on Cu_s^{+2} or Cu_s^0 sites. Consequently, with this new information, it may be possible that a judicious combination of these surface reactions, coupled with H_2 and CO chemisorption, could not only count all surface metal atoms but also distinguish between the two metals at the surface, thus providing the characterization capability desired. This paper describes our initial efforts with a dispersed Pt–Cu system.

EXPERIMENTAL

The SiO_2 (Davison 57, S.A. = 220 m^2/g, 60/80 mesh) was calcined at 773 K for 4 h in flowing O_2 (MG Ind., 99.999%) at 1.5 L/min before being used to prepare samples, and a 0.78% Pt/SiO_2 catalyst was prepared using an ion exchange technique in which the SiO_2 was stirred in an aqueous solution of $Pt(NH_3)_4Cl_2$ (Aldrich, 99.99%), as described in detail elsewhere (34). An incipient wetness method was employed to prepare a 1.96% Cu/SiO_2 catalyst (36). Silica-supported, bimetallic Cu–Pt catalysts having Cu amounts of 2.16 and 3.41% were prepared by impregnating a portion of the 0.78% Pt/SiO_2 catalyst, after reduction in H_2, with an aqueous solution of $Cu(NO_3)_2 \cdot xH_2O$ (Alfa, 99.999%) according to the following procedure: (a) reduce 0.78% Pt/SiO_2 at 673 K for 1 h in flowing H_2 (MG Ind., 99.999%) at 32 cm^3 (STP)/min; (b) evacuate, cool, and passivate at 300 K for 30 min under a constant pressure of about 160 Torr of O_2; (c) impregnate the reduced Pt/SiO_2 sample dropwise with the Cu solution corresponding to an amount of water sufficient to fill the pore volume of the SiO_2 (0.6 cm^3/g), and (d) dry the resulting material at 393 K in air overnight. The dried sample was then stored in a desiccator. Details of such a catalyst preparation have been given previously (15). Although slightly less than 0.78 wt% Pt, this designation will still be used in the two bimetallic catalysts to clarify their origin.

Measurements of N_2O, CO, or H_2 adsorption on the monometallic and bimetallic catalysts were conducted in the same volumetric system employed earlier (34–36, 43), and the uncertainty of the reported uptakes is ±0.2 μmol/g. The 1.96% Cu/SiO_2 catalyst was reduced *in situ* in a chemisorption cell using one of the pretreatment protocols described in Table 1. In this study, the two low-temperature reduction (LTR) procedures are designated as either pretreatment I (LTR473 or 573) or II (LTR473 or 573) to distinguish them from the earlier higher temperature reduction (HTR) at 673 K used previously (34, 35), and they were used with the Cu-containing catalysts. The 0.78% Pt/SiO_2 sample first underwent the same reduction procedure at 673 K as that used previously for a 0.81% Pt/SiO_2 catalyst (34, 35). All gas flow rates during the sample pretreatment were maintained at 32 cm^3(STP)/min with Tylan Model FC 260 mass flow controllers. Prior to admitting any gas into the adsorption system, the N_2O (BOC, medical grade, 99.9%), CO (Matheson, 99.99%), and the H_2, Ar, or He (MG Ind., 99.999%) were purified using a moisture trap and/or an Oxy-trap (Alltech), as described earlier (34). Isotherms for H_2 adsorption at 300 K were then obtained.

The 1.96% Cu/SiO_2 catalyst was routinely reduced using pretreatment I (LTR473), and a set of CO isotherms was first obtained at 300 K and pressures ranging from

TABLE 1

Pretreatment Protocols for Silica-Supported Cu and Cu–Pt Catalysts

Pretreatment I (LTR)

1. Heat to either 473 or 573 K and hold for 1 h in flowing He (1 atm).
2. Reduce in flowing H_2 (1 atm) for 4 h at either 473 or 573 K.
3. Evacuate at either 473 or 573 K for 30 min.
4. Cool to 300 K and continue evacuation for 1 h.

Pretreatment II (LTR)

1. Reheat to either 473 or 573 K and hold for 1 h in flowing H_2 (1 atm) after using pretreatment I (LTR).
2. Evacuate at either 473 or 573 K for 30 min.
3. Cool to 363 K in vacuum.
4. Expose to 10% N_2O (0.1 atm) at 363 K for 30 min.
5. Evacuate at 363 K for 30 min.
6. Cool to 300 K and continue evacuation for 1 h.

40 to 350 Torr. This sample was then heated to 473 K and held for 1 h in flowing H_2 (1 atm), following steps (1) and (2) listed under pretreatment I (LTR473) given in Table 1, and H_2 uptakes were measured at 300 K. The catalyst was then given pretreatment II (LTR473) to convert Cu^0 surface atoms to Cu^{+1} sites via exposure to N_2O at 363 K and to provide a monolayer of "Cu_2O," and then another set of CO isotherms was obtained. The irreversible CO adsorption on either a reduced or an oxidized Cu surface was determined by the difference between the two isotherms (44). After another pretreatment II (LTR473), hydrogen adsorption on the "Cu_2O" surface was measured. Extrapolation of the linear portion (between 150 and 250 Torr) of both the total and reversible H_2 isotherms to zero pressure (to correct for reversible adsorption on the support) gave the two uptake values used to calculated irreversible adsorption on either a reduced or oxidized copper surface. When a LTR573 pretreatment was used, the same procedure was used to acquire isotherms after this pretreatment.

The Cu–Pt bimetallic catalysts were first given pretreatment II (LTR573) to deposit O atoms on the metal surfaces via N_2O decomposition at 363 K, and the H uptakes at 300 K over pressures ranging from 50 to 350 Torr were determined by the "H_2–N_2O titration" technique discussed earlier (34). In these cases, the total H uptakes were estimated based on the slope of the isotherm parallel to that of the reversible isotherm. The Cu–Pt catalyst was subjected again to pretreatment II (LTR573), and the "CO–N_2O titration" technique, which was recently demonstrated with a 0.81% Pt/SiO_2 catalyst, was employed (34, 35). Isotherms for both CO and H_2 adsorption at 300 K were also obtained after using procedure I (LTR573). Finally, hydrogen titration of O atoms on Pt at either 200 or 220 K following exposure to N_2O at 363 K was conducted to minimize or eliminate any H spillover from the Pt to the Cu_2O surface. The H_2 titration reaction proceeds readily on Pt at these temperatures (45). The sample cell was placed into a slush bath and prepared according to the method described by Rondeau (46), using either trichloroethylene (Fluka, 99%) or *n*-octane (Fluka, 96%) and adding liquid nitrogen to the slush bath periodically to maintain constant temperature.

Chemisorption of CO on 1.96% Cu/SiO_2 at 300 K was independently determined using a gravimetric system described earlier (34–36). An appropriate amount (ca. 7–9 mg) of the Cu-only catalyst was placed in the sample pan in the TGA system and reduced *in situ* at 473 K for 4 h in a flowing mixture of 30% H_2/70% Ar at a rate of 60 cm^3(STP)/min according to pretreatment I (LTR473), but using a purge of pure Ar rather than evacuation to remove hydrogen. After cooling to 300 K, a gas mixture of 10% CO in Ar was flowed over the reduced sample at 300 K for 30 min, then this gas stream was switched to pure Ar to remove reversibly adsorbed CO. The net weight change then corresponded to the irreversible CO adsorption (CO_{irr}). The catalyst was then given pretreatment II (LTR473) and the net weight gain due to the conversion of the metallic Cu^0 surface to "Cu_2O" during this step was measured. The catalyst was cooled to 300 K in pure flowing Ar and CO chemisorption on the Cu^{+1} surface was conducted using a flow of 10% CO/90% Ar. After reduction at 473 K, the sample was given pretreatment I (LTR573) following the above procedure and irreversible CO adsorption at 300 K was measured. Coverages of CO and O on the bimetallic Cu–Pt samples were obtained in the same fashion as for the Cu-only catalyst. All gases were purified in a manner quite similar to that used in the volumetric system, although special purification of the Ar was employed in this gravimetric system (34).

Prior to characterization by X-ray diffraction (XRD), each catalyst was given pretreatment I (LTR473 or 573), after which the reduced sample was exposed to a gas mixture of 1% O_2 in flowing Ar for 1 h at 300 K for passivatation. Each XRD pattern of a passivated sample was collected *ex situ* using a Rigaku *Geigerflex* diffractometer with a Cu $K\alpha(\lambda = 1.5418$ Å) radiation source and a graphite monochromator. The respective X-ray tube voltage and current during the data collection were 40 kV and 20 mA. The air-exposed sample was loaded into a thin quartz holder with a 2-cm^2 window in the diffractometer and scanned from a 2θ value of 10–80° at a rate of 5°/min. When peaks around $2\theta = 35.3°$ (CuO), 36.5° (Cu_2O), or 43.3° (Cu^0) were observed in the case of 1.96% Cu/SiO_2 catalyst, a slower scan of 1°/min was used to improve peak resolution. In a similar way, XRD patterns were collected for the two reduced, passivated Cu–Pt catalysts to determine crystallite sizes of Cu and Pt as well as to see if any alloying could be detected after reduction at 573 K. Average crystallite sizes for each metal were determined using the Scherrer equation with Warren's correction.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), using a Mattson Research Series 10000 spectrometer with a Harrick Scientific-DRA diffuse reflection cell, was employed to examine CO adsorbed on these catalysts. Details of this system, which allows *in situ* sample pretreatment, have been provided elsewhere (34, 47). A sample of the 3.4% Cu–0.78% Pt catalyst (0.12 g) was loaded into the infrared cell and given pretreatment II (LTR573) to oxidize the Cu surface to Cu_2O and to chemisorb oxygen atoms on any surface Pt^0 atoms. An interferogram of this oxidized sample was first obtained at 300 K to be used as a reference spectrum. The sample was then exposed to a flowing mixture of 10% CO (76 Torr) in He for 30 min and purged with He before a second interferogram was acquired and Fourier transformed. Spectra of CO adsorbed on the 1.96% Cu/SiO_2 catalyst after pretreatment II (LTR573) were collected in the same fashion. All interferograms were a composite of 1000 scans recorded with a resolution of 4 cm^{-1}. All gases used were purified as described previously and maintained at a total flow rate of 20 cm^3(STP)/min.

RESULTS

The irreversible uptakes of CO on the 1.96% Cu/SiO$_2$ catalyst at 300 K were determined after different reduction temperatures, i.e., 473 and 573 K, and the amount after LTR473 was 4.2 μmol/g while the uptake after an LTR573 step was 1.7 μmol/g, as shown in Table 2. The volumetric and gravimetric results are in good agreement. The CO$_{irr}$ uptake at 300 K increased to 23.3 μmol/g after the Cu surface reduced at 473 K was exposed to N$_2$O at 363 K, with the net increase being due to the conversion of Cu$_s^0$ atoms into Cu$_s^{+1}$ sites, on which CO chemisorbs much more strongly at 300 K compared to Cu$_s^0$ and Cu^{+2} sites (36, 41, 42). The capacity of this catalyst to chemisorb CO at 300 K decreased after reduction at 573 K, indicating a loss of Cu^{+1} sites, and the CO$_{irr}$ adsorption on "Cu$_2$O" after pretreatment LTR573 of 8.9 μmol/g was also lower than that after reduction at 473 K, as indicated in Table 2. No irreversible CO adsorption at 300 K was detected on the pure SiO$_2$ (34). Typical sets of isotherms for CO adsorption are displayed in Fig. 1.

Some irreversible hydrogen adsorption occurred at 300 K (10.4 μmol of H$_2$/g) on 1.96% Cu/SiO$_2$ after reduction at 473 K, in agreement with earlier results showing appreciable H chemisorption on silica-supported Cu (15, 22), but after exposure to N$_2$O (pretreatment II (LTR473)) no H$_2$ adsorption was detected, as demonstrated in Fig. 2. It is our contention that the H$_2$–N$_2$O titration reaction, established with Pt/SiO$_2$ (34), can provide a useful approach to counting only Pt$_s$ sites in bimetallic Cu–Pt catalysts as long as no reduction of Cu^{+1} species occurs due to H spillover from the Pt surface. Adsorption of H$_2$ on pure SiO$_2$ clearly obeyed Henry's law, giving no irreversible adsorption and less than 0.3 μmol/g of total uptake at 350 Torr and 300 K, consistent with adsorption on SiO$_2$ (48, 49).

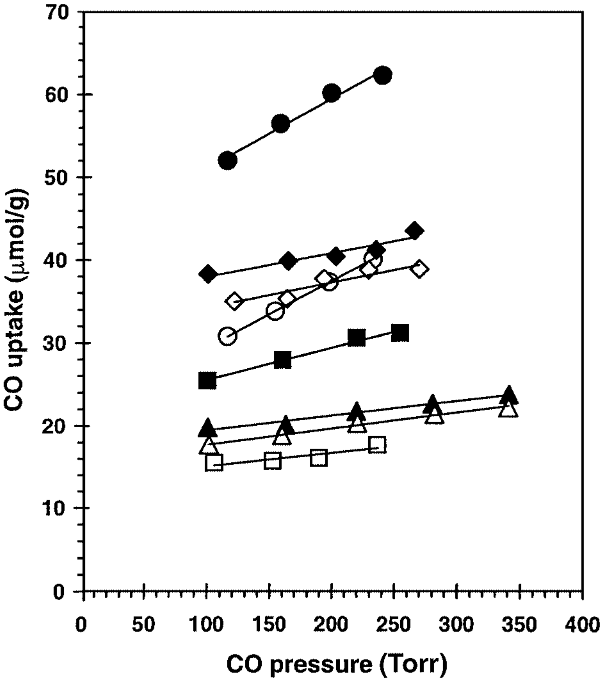

FIG. 1. Isotherms for CO adsorption on 1.96% Cu/SiO$_2$ catalyst after different pretreatments: I (LTR473)—◆, ◇; II (LTR473)—●, ○; I (LTR573)—▲, △; II (LTR573)—■, □. Open and closed symbols represent the respective total and reversible gas uptakes at 300 K.

Following CO chemisorption at 300 K on 1.96% Cu/SiO$_2$, the sample was again given pretreatment I (LTR473) and the amount of oxygen adsorption at 363 K was determined gravimetrically to provide a direct measurement of the

TABLE 2

Adsorption of N$_2$O at 363 K and H$_2$ and CO at 300 K on Silica-Supported Pt or Cu Catalysts

		Gas uptake (μmol/g)				Surface concentration (μmol/g)^b (vol)				
		Volumetric		Gravimetric				Cu$_s^0$		
Catalyst	Pretreatment^a	H$_{2Tot}$	CO$_{Irr}$	CO$_{Irr}$	O$_{Irr}$^{c}	Pt$_s$	Cu$_s^{+1}$	ΔCO$_{irr}$^{d}	2O	Cu$_s$
0.78% Pt/SiO$_2$	I (HTR)	11.5				23.0				
1.96% Cu/SiO$_2$	I (LTR473)	10.4^e							20.8^f	
	I (LTR473)		4.2	3.9	9.5		4.2	19.1	19.0	23.2
	II (LTR473)		23.3	21.0			23.3			23.3
	II (LTR473)	0.0								
	I (LTR573)		1.7	2.1	3.8		1.7	7.2	7.6	9.3
	II (LTR573)		8.9	11.1			8.9			8.9

[a] See Table 1.

[b] Assuming H/Pt$_s$ = CO$_{irr}$/Cu$_s^{+1}$ = O/2 Cu$_s^0$ = 1.

[c] Atomic O uptake after exposure to N$_2$O at 363 K and 76 Torr.

[d] ΔCO$_{irr}$ between pretreatments I and II.

[e] Assuming H$_{irr}$/Cu$_s^0$ = 1.

[f] Irreversible.

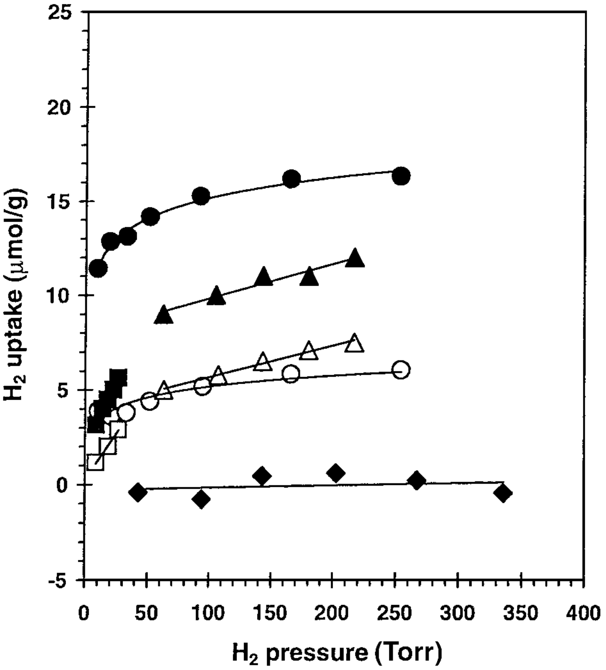

FIG. 2. Isotherms for H_2 adsorption on Cu/SiO_2 catalysts after different pretreatments: 1.96% Cu/SiO_2 I (LTR473)—●, ○ and II (LTR473)—◆; 4.32% Cu/SiO_2 reduced at 673 K (Ref. 15)—▲, △; 5% Cu/SiO_2 reduced at 623 K (Ref. 22)—■, □. Open and closed symbols represent the respective total and reversible gas uptakes at 300 K.

extent of "Cu_2O" formation. A net weight gain appeared after introduction of 76 Torr of N_2O into the TGA system, as shown in Fig. 3, which was equal to 9.5 μmol of O_{irr}/g, thus giving 19.0 μmol of Cu_s^0/g (34–36). After cooling to 300 K in pure flowing He, CO was chemisorbed at 300 K to give an irreversible weight gain of 6.6 μg, as indicated in Fig. 3, which corresponded to a CO_{irr} uptake of 21.0 μmol/g. A similar set of measurements was done with a sample of 1.96% Cu/SiO_2 after reduction at a higher temperature of 573 K, and the results are also listed in Table 2.

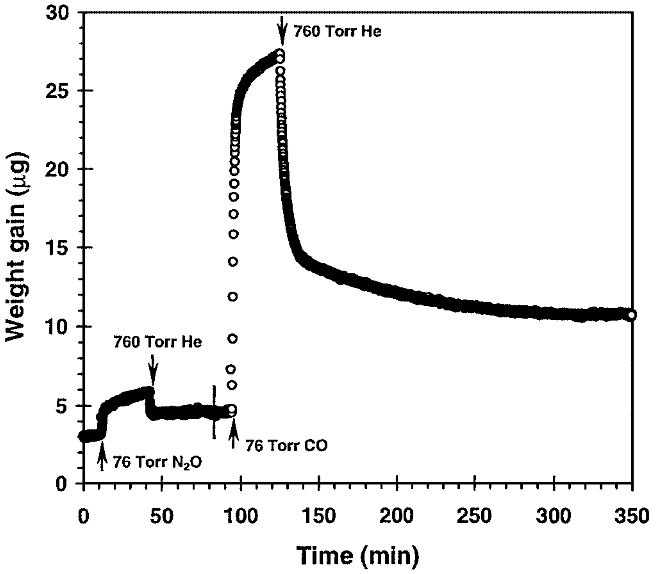

FIG. 3. Gravimetric measurements for dissociative N_2O adsorption at 363 K on 1.96% Cu/SiO_2 after reduction at 473 K followed by CO adsorption at 300 K on the oxidized surface. The vertical solid bar differentiates the two adsorption steps.

For the 1.96% Cu/SiO_2 catalyst after a chosen pretreatment, the surface concentrations of Cu^{+1} and Cu^0 were calculated based on both volumetric and gravimetric uptake values, which were in good agreement, and they are included in Table 2. The crystallite size, d, for metallic Cu was calculated based on X-ray line broadening and compared with that calculated only for Cu^0 using the correlation d (nm) $= 1.1/(2O_{irr}/Cu_{tot})$ (15, 38–40). When including Cu_s^{+1} sites in the total number of surface Cu_s atoms, an overall crystallite size was approximated by d (nm) $= 1.15\ Cu_s/Cu_{tot} = 1.15/[CO_{irr} + 2O_{irr}/Cu_{tot}]$ (36 and references therein). These results are shown in Table 3, and the results for metallic Cu^0 are especially consistent. Since the

TABLE 3

Metal Dispersion and Crystallite Size in Silica-Supported Pt or Cu Catalysts

		Dispersion						Crystallite size, d (nm)						
								Volumetric or gravimetric				XRD		
Catalyst	Pretreatment	Pt_s (H_{tot}/Pt_{tot})	Cu_s^0 (H_{irr}/Cu_{tot})	Cu_s^0 ($\Delta CO_{irr}{}^a/Cu_{tot}$)	Cu_s^0 ($2O_{irr}/Cu_{tot}$)	Cu_s^{+1} (CO_{irr}/Cu_{tot})	Cu_s	Pt^b	$(Cu^0)^{a,c}$	$(Cu^0)^c$	$(Cu^{+1} + Cu^0)^d$	Pt	Cu_2O	Cu^0
0.78% Pt/ SiO_2	I (HTR)	0.58						2.0				ND		
1.96% Cu/ SiO_2	I (LTR473)		0.067											
	I (LTR473)				0.062	0.076	0.076		18	18	15		ND	16
	II (LTR473)			0.062							15			
	II (LTR473)		0.0											
	I (LTR573)				0.025	0.006	0.031		47	45	37		ND	32
	II (LTR573)			0.023		0.029	0.029				39			

[a] Based on ΔCO_{irr} between pretreatments I and II.

[b] Assuming d_p (nm) $= 1.13/(H_{tot}/Pt_{tot})$.

[c] Based on O_{irr} at 363 K.

[d] Assuming an average correlation of d_p (nm) $= 1.15/[(CO_{irr} + 2O_{Irr})/Cu_{tot}]$ for Cu_2O and Cu^0.

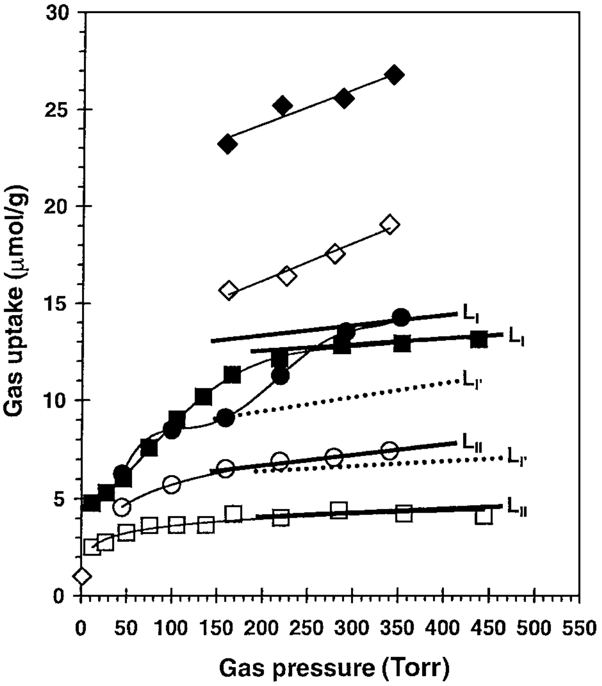

FIG. 4. Titration isotherms for 2.2% Cu–0.78% Pt/SiO$_2$ after pretreatment II (LTR573): H$_2$ titration at 300 K and 50–350 Torr—●, ○; H$_2$ titration at 300 K and 10–440 Torr—■, □; CO titration at 300 K—◆, ◇. Each L'_I line was obtained by extrapolation through the inflection point of each total adsorption isotherm (L_I) parallel to the slope of the corresponding reversible isotherm (L_{II}). Open and closed symbols represent the respective total and reversible gas uptakes at 300 K.

behavior of a comparable 0.81% Pt/SiO$_2$ catalyst has already been published regarding both H$_2$ and CO titration following N$_2$O exposure (34, 35), only the H uptake on the 0.78% Pt/SiO$_2$ catalyst is reported in Table 2.

The titration by H$_2$ or CO of chemisorbed oxygen provided by the decomposition of N$_2$O, which we designate "H$_2$–N$_2$O titration" or "CO–N$_2$O" titration, respectively, was first applied to the 2.2% Cu–0.78% Pt/SiO$_2$ catalyst using pretreatment II (LTR573); in addition, both CO and H$_2$ chemisorption following reduction at 573 K was measured. A stable uptake was not rapidly achieved during H$_2$ titration and an apparent pressure dependence was indicated by an inflection point, which is visible in Fig. 4. It is quite possible that this additional uptake is due to the reduction of the "Cu$_2$O" phase via H spillover from Pt$_s$ sites (50, 51), especially since small amounts of adsorbed H$_2$O can facilitate this step (50) and the isotherm for reversible adsorption exhibited normal adsorption behavior. Monolayer H coverages on Pt$_s$ atoms after titration is achieved above 100 Torr (45); so if the uptake between 100 and 150 Torr is associated only with Pt$_s$, then an estimate of these sites can be obtained by extrapolating a line parallel to the reversible isotherm (L_{II}) through the inflection point ($L_{I'}$), and these results are summarized in Table 4. The CO titration of chemisorbed oxygen following exposure to N$_2$O at 363 K gave a value of 8.5 μmol/g for CO irreversibly adsorbed on the bimetallic catalyst after pretreatment II (LTR573), which represents the total number of Pt$_s^0$ and Cu$_s^{+1}$ sites (34, 35), and a typical set of CO titration isotherms is provided in Fig. 4. This CO$_{irr}$ uptake for the titration of O$_{irr}$ atoms increased when the catalyst was exposed to N$_2$O at temperatures higher than 393 K, as also shown in Table 4, which may be the result of additional subsurface oxidation of Cu^0.

Unfortunately, hydrogen titration at 300 K of O atoms on Pt$_s$ deposited during pretreatment II (LTR573) seemed to be combined with H spillover from Pt to "Cu$_2$O" surfaces; thus it could not give unambiguous quantification of the number of Pt$_s$ sites present in these bimetallic catalysts. To inhibit or eliminate the migration of H atoms, the titration reaction was conducted at temperatures which were much lower, 210 ± 10 K, but which were still high enough to allow the titration reaction on Pt to occur (45). This revealed a total adsorption capacity of only 6.1 μmol/g. Irreversible CO adsorption at 300 K on this catalyst after reduction at 573 K was 5.0 μmol/g, while the total and irreversible H$_2$ uptakes at 300 K were 8.3 and 2.5 μmol H$_2$/g, respectively. It is obviously difficult to readily distinguish H atoms chemisorbed on Pt$_s$ atoms from those on Cu$_s^0$ sites, not only because H coverages on Cu$_s^0$ at 300 K can be significant, as previously shown for 1.96% Cu/SiO$_2$, but also because H adsorption on Cu can be facilitated by the presence of a Group VIII metal (22, 23). Typical isotherms are shown in Fig. 5, and values for CO and H$_2$ chemisorption on the

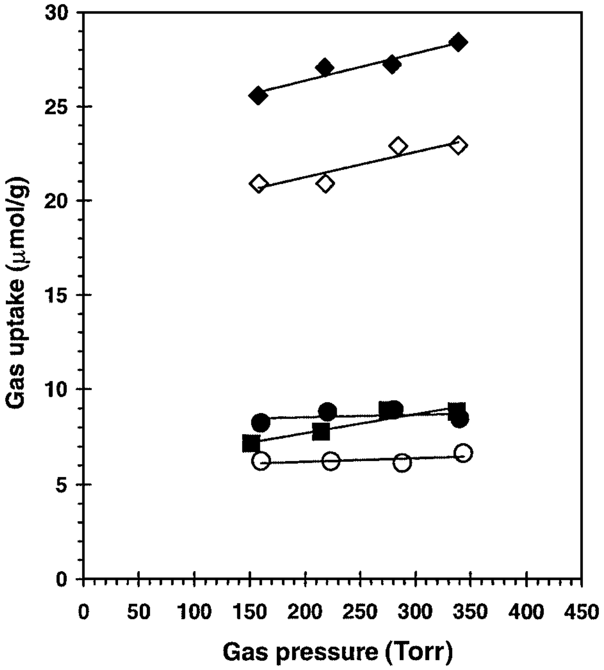

FIG. 5. Isotherms on 2.2% Cu–0.78% Pt/SiO$_2$ after either pretreatment I (LTR573) or II (LTR573): I (LTR573), H$_2$ adsorption at 300 K—●, ○; II (LTR573), H$_2$ titration at 200 K—■; I (LTR573), CO adsorption at 300 K—◆, ◇. Open and closed symbols represent the respective total and reversible uptakes.

TABLE 4

Adsorption of N_2O at 363 K and H_2 and CO at 300 K on SiO_2-Supported Cu–Pt Catalysts

Catalyst	Pretreatment	Gas uptake (μmol/g)								Surface concentration (μmol/g)[a]	
		Volumetric					Gravimetric			Pt_s based on H_2–N_2O titr.	Cu_s based on (CO–N_2O titr.)–$Pt_{S_{ave}}$
		H_2–N_2O titr.									
		Tot. H_2 based on		Irr. H_2 based on L_I–$L_{I'}$	CO_{irr}	CO–N_2O titr.	O_{irr}[c]	CO_{irr}	CO–N_2O titr.		
		L_I	$L_{I'}$[b]								
2.2% Cu–0.78% Pt	I (LTR573)	8.3		2.5[d]							
	I (LTR573)				5.0			4.6		5.0[e]	
	II (LTR573)	12.4	8.2	4.2						5.5	
	II (LTR573)	12.8	7.2	5.6						4.8	
	II (LTR573)	12.3	6.0 (7.1_{ave})	6.3						4.0	
	II (LTR573)	6.1								4.1[f]	
	II (LTR573)					8.5			9.2[g] (180 μg/gcat)	4.7_{ave}	3.8 (vol) 4.3 (grave)
	I (LTR573)						6.8				
	II (LTR573)					14.9				4.7_{ave}	10.2
3.4% Cu–0.78% Pt	I (LTR573)	10.2		6.1[d]							
	I (LTR573)				3.6			3.8		3.6[e]	
	II (LTR573)	8.1		6.2						(5.4)	
	II (LTE573)	5.3								3.5[f]	
	II (LTR573)					8.4			8.7[h] (190 μg/gcat)	3.6_{ave}	4.8 (vol) 5.2 (grav)
	I (LTR573)						6.1				
	II (LTR573)					15.5[i]				3.6_{ave}	11.9

[a] Assuming $H/Pt_s = CO_{irr}/Cu_s^{+1} = O/2Cu_s^0 = 1$ (see text).
[b] Extrapolating $L_{I'}$ parallel to L_{II} in Fig. 4 (●, ○).
[c] Atomic O uptake after exposure to N_2O at 363 K and 76 Torr.
[d] Based on L_I–L_{II}.
[e] Assuming no Cu^{+1} species after reduction at 573 K for 4 h.
[f] Assuming H_2 adsorption on Pt_s sites only at either 200 or 220 K.
[g] Assuming 4.7 μmol of Pt_s.
[h] Assuming 3.6 μmol of Pt_s.
[i] After exposure to N_2O at 393 K and 76 Torr.

reduced surface are included in Table 4 for comparison to the titration results.

A similar titration and chemisorption sequence was extended to the 3.4% Cu–0.78% Pt/SiO_2 catalyst after reduction at 573 K. First, hydrogen titration was measured at 300 K after N_2O decomposition at 363 K, giving total and irreversible uptakes of 8.1 and 6.2 μmol H_2/g. Again, the number of total metal surface sites was obtained from the CO titration reaction, which gave 8.4 μmol/g. Exposure of this catalyst to N_2O at 393 K, rather than 363 K, again produced a higher uptake value for CO titration at 300 K. Hydrogen titration at 220 K, rather than 300 K, on this catalyst using the same pretreatment II (LTR573) gave a total H_2 uptake of 5.3 μmol/g. Finally, both H_2 and CO uptakes were determined for the catalyst after reduction at 573 K. All these volumetric results are shown in Table 4.

In the fashion used for the 1.96% Cu/SiO_2 catalyst, the extent of oxygen chemisorption via dissociative N_2O adsorption at 363 K as well as irreversible CO adsorption at 300 K on the oxidized surface layer was gravimetrically determined after the Cu–Pt catalysts had undergone pretreatment II (LTR573). Weight gains for 2.2% Cu–0.78% Pt/SiO_2 during N_2O decomposition at 363 K and the subsequent CO titration at 300 K corresponded to 6.8 and 9.3 μmol/g, respectively, for the respective O_{irr} and CO_{irr} coverages, and similar amounts were obtained with 3.4% Cu–0.78% Pt/SiO_2. All gravimetric results are also listed in Table 4.

In situ DRIFT spectra of CO adsorbed on 3.4% Cu–0.78% Pt/SiO_2 after different pretreatments are shown in Fig. 6. After pretreatment I (LTR573), a subsequent He purge following exposure to CO gave only one peak, at 2061 cm^{-1} (Fig. 6c). When 76 Torr CO was introduced into the catalyst at 300 K after the surface had been covered by chemisorbed oxygen via N_2O decomposition at 363 K, bands at 2121 and 2061 cm^{-1} were observed after purging (Fig. 6d). The 2061-cm^{-1} peak was unchanged in position after N_2O decomposition, but it became somewhat less intense. To verify the band assignments, spectra were acquired of CO adsorbed on 1.96% Cu/SiO_2 at 300 K after pretreatment II (LTR473). Only a single peak on this oxidized Cu surface, centered at 2128 cm^{-1}, appeared after

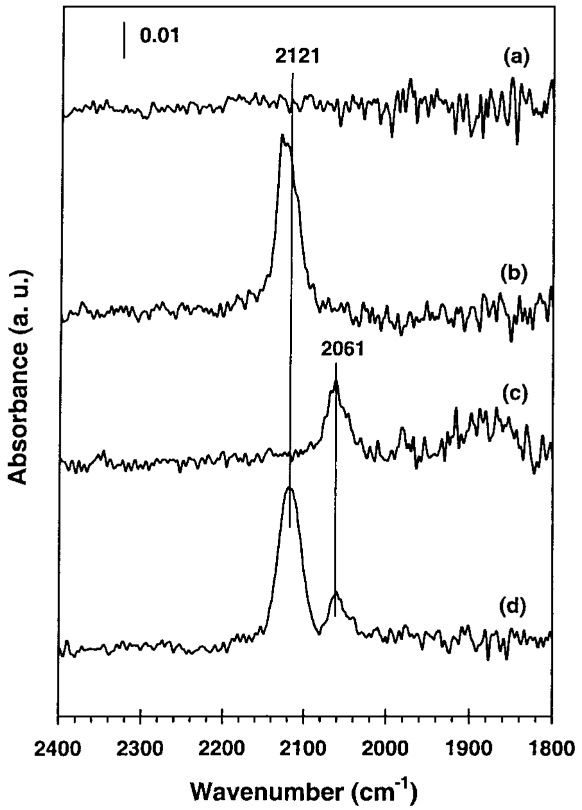

FIG. 6. DRIFT spectra of CO irreversibly adsorbed at 300 K on silica-supported metals after different pretreatments: (a) pure SiO_2 after procedure I (LTR573), (b) 1.96% Cu/SiO_2 after procedure II (LTR573), (c) 3.4% Cu–0.78% Pt/SiO_2 after procedure I (LTR573), (d) 3.4% Cu–0.78% Pt/SiO_2 after procedure II (LTR573). All spectra were recorded after a 30-min purge with He at 300 K.

purging (Fig. 6b). In these spectra, the peaks near 2125 cm^{-1} represent CO associated with Cu^{+1} sites (see 36, and references therein) while the 2061-cm^{-1} bands are assigned to linearly adsorbed CO on Pt_s atoms at the Cu–Pt surface (52–59). No CO absorption bands were observed after exposure of pure SiO_2 to CO (Fig. 6a).

XRD patterns were obtained for passivated, reduced Cu–Pt catalysts as well as for the Cu-only and Pt-only catalysts, and these are provided in Fig. 7, while the crystallite sizes determined for the two metals via XRD line broadening are given in Table 5. Neither of the bimetallic catalysts gave detectable diffraction lines for CuO or Cu_2O, and only peaks for metallic Cu and Pt phases were observed at the respective 2θ values of 43.26 and 39.85° for the most intense reflections.

DISCUSSION

A 0.81% Pt/SiO_2 catalyst with a dispersion of 0.61, prepared identically to the 0.78% Pt/SiO_2 catalyst used here, has been thoroughly characterized using the volumetric, gravimetric, XRD, and *in situ* DRIFTS techniques described earlier (34, 35). This established the behavior for the latter catalyst, used as our base catalyst, which had a very similar dispersion, 0.58. The SiO_2 adsorbs no CO, irrespective of reduction temperature (34); thus any CO chemisorption on the 1.96% Cu/SiO_2 catalyst at 300 K is associated with Cu species. At 300 K CO is not strongly adsorbed on surface Cu^0 and Cu^{+2} sites because the heat of adsorption is low (<9.3 kcal/mol), but irreversible adsorption does occur on Cu^{+1} surfaces (36, 41, 42). Dissociative adsorption of N_2O on Cu^0 surfaces at selected conditions creates a surface monolayer of adsorbed oxygen with a Cu_2O composition (36–40). Although there is uncertainty regarding the extent of hydrogen chemisorption on metallic Cu surfaces around 300 K, it has been unequivocally demonstrated on dispersed Cu crystallites (15, 22, 60–62).

The amounts of irreversibly adsorbed CO on 1.96% Cu/SiO_2 after a given pretreatment are indicative of Cu^{+1} species, and they reveal that a fraction of Cu remains in an unreduced state (36); consequently, this offers a volumetric technique to indirectly measure the surface Cu^0 population; i.e., the differences in CO_{irr} uptakes before and after surface oxidation by N_2O at 363 K would give this value, and they are listed in Table 2. Another method for measuring Cu^0_s atoms in a Cu-only sample is a gravimetric technique

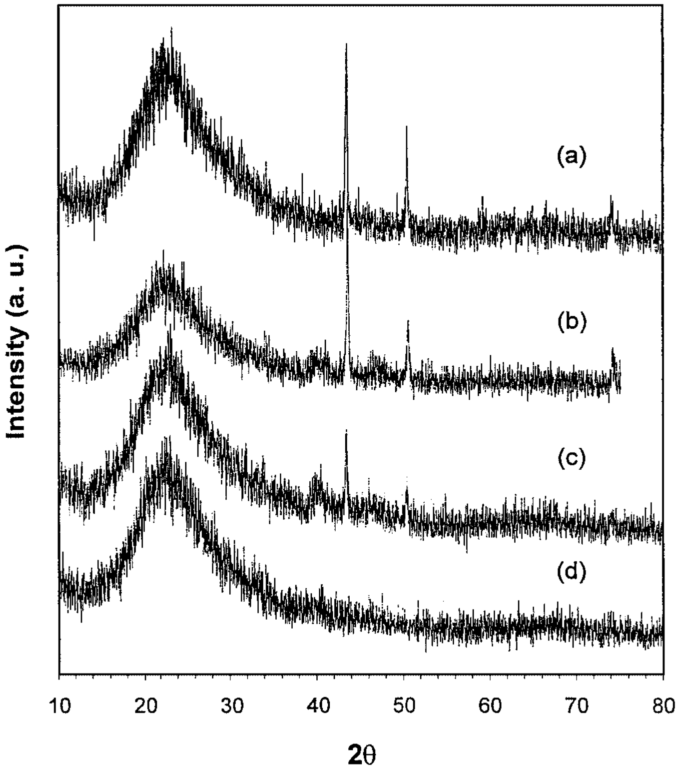

FIG. 7. X-ray diffraction patterns for SiO_2-supported Cu, Pt, and bimetallic Cu–Pt catalysts reduced at 573 K: (a) 1.96% Cu/SiO_2, (b) 3.4% Cu–0.78% Pt/SiO_2, (c) 2.2% Cu–0.78% Pt/SiO_2, (d) 0.78% Pt/SiO_2. The principal Pt peak is at 39.85° and Cu peaks can be seen at 43.26° and 50.34°.

TABLE 5

Apparent Dispersions and Crystallite Sizes of Pt and Cu in SiO_2-Supported Bimetallic Catalysts

					Crystallite size, d_p (nm)				
		Pt dispersion based on		Cu dispersion based on	Volumetric or gravimetric		XRD		
Catalyst	Pretreatment	H_{tot}/Pt_{tot}	CO_{irr}/Pt_{tot}	$[(CO–N_2O_{titr})–Pt_s]Cu_{tot}$	Pt[a]	(Cu^0)[b]	Pt	Cu_2O	Cu^0
2.2% Cu–0.78% Pt	I (LTR573)	0.12[c]			9.0		7.1	ND	
	I (LTR573)		0.12 (vol)		9.0				
	I (LTR573)		0.11 (grav)		9.8				
	II (LTR573)	0.12[d]			9.0				
	II (LTR573)	0.10[e]			11.3				
	II (LTR573)			0.010		110			29
	II (LTR573)[f]			0.029		38			
3.4% Cu–0.78% Pt	I (LTR573)	0.30[c]					13	ND	
	I (LTR573)		0.090 (vol)		13				
	I (LTR573)		0.095 (grav)						
	II (LTR573)	0.13[d]			12				
	II (LTR573)	0.09[e]			13				
	II (LTR573)			0.0090	12.6	120			37
	I (LTR573)				11.9				
	II (LTR573)[f]			0.022	12.6	49			

[a] Assuming d_p (nm) $= 1.13/D$, where D is either H_{tot}/Pt_{tot} or CO_{irr}/Pt_{tot}.

[b] Assuming d_p (nm) $= 1.10/D$, where $D = [(CO–N_2O_{titr})–Pt_s]/Cu_{tot}$.

[c] Using H_{irr}/Pt_{tot}.

[d] Average titration value from Table 4.

[e] Titration at ~210 K.

[f] After exposure to N_2O at 393 K and 76 Torr.

(36, 37) in which the O_{irr} uptake during dissociative N_2O adsorption at 363 K is directly measured and ascribed to surface Cu^0 atoms using an O_{irr}/Cu^0_s adsorption ratio of 0.5 (36, 38–40). There is excellent agreement between the two approaches, as seen in Tables 2 and 3. The respective volumetric and gravimetric values for Cu^0_s are 19.1 vs 19.0 μmol/g after reduction at 473 K and 7.2 vs 7.6 after reduction at 573 K. The Cu crystallite sizes based on these values are also very consistent with the sizes calculated from the XRD data, such as that in Fig. 7a, as indicated in Table 3. No Cu_2O XRD peaks would be observable if this phase existed either as a monolayer on the surface of metallic Cu particles or as very small Cu_2O particles strongly interacting with the SiO_2 surface to prevent their reduction. This model is supported by the unreasonably large crystallites predicted if all Cu_2O existed as spherical (or hemispherical) particles, i.e., 90- or 200-nm Cu_2O crystallites based on CO uptakes after reduction at 473 or 573 K, respectively. Consequently, the Cu in the 1.96% Cu/SiO_2 sample might be visualized as relatively large particles of metallic Cu covered by a monolayer of "Cu_2O" existing together with highly dispersed Cu^{+1} species on the silica surface.

Dissociative chemisorption of H_2 on metallic copper surfaces is activated, with activation barriers from 3 to 10 kcal/mol having been reported (15, 62, and references therein). Based on recent results, heats of adsorption falling between 6 and 9 kcal/mol can be estimated using desorption energies of 15–18 kcal/mol (60–62); consequently, irreversible adsorption (per the working definition used here) on Cu is possible, and the isotherms in Fig. 2 verify it can be observed, as reported previously (15, 22). Hydrogen adsorption on single crystals indicates dissociative adsorption occurs more readily on high-index Cu planes, such as Cu(211), (311), and (755) surfaces, compared to low-index planes (63); thus H adsorption may occur more readily on small Cu crystallites. It may be a coincidence, but if an adsorption stoichiometry of $H_{irr}/Cu^0_s = 1$ is assumed, excellent agreement is obtained with the other methods used to count Cu^0_s sites (see Table 2). Characterization of Cu catalysts by H_2 chemisorption was not pursued, but the results do provide evidence that H chemisorption in bimetallic Cu systems such as this one can be complicated by adsorption on both metals, as previously shown (22), and interpretation of H_2 uptakes alone must be made with caution. It is clear, though, that no irreversible H_2 adsorption occurs on Cu^{+1} sites (see Table 2); therefore, another metal, such as Pt, is required for any possible reaction with "Cu_2O" to occur via H spillover.

Dissociative N_2O adsorption at appropriate temperature and pressure conditions has been used to determine the metal surface area of reduced Cu (36, 38–40) and Ag catalysts (64, 65). This decomposition reaction on a Pt/SiO_2 catalyst has now been investigated and combined with H_2 or CO titration at 300 K (H_2–N_2O titration and CO–N_2O

titration) to count Pt_s atoms (34, 35). The findings of this initial investigation are summarized by Eqs. [1]–[3]. These results are consistent with gravimetric measurements of oxygen chemisorption at 363 K (34) after which the CO–N_2O titration reaction was conducted at 300 K (35). The net weight gain was consistent with that predicted from the volumetric results. At 300 K hydrogen does not chemisorb irreversibly on Cu surfaces covered by O atoms, as demonstrated with the 1.96% Cu/SiO_2 catalyst. This allows the possibility that the H_2–N_2O titration reaction on a bimetallic Pt–Cu surface could measure only the Pt_s sites, provided no other complicating factors exist.

Unfortunately, the additional H_2 uptakes on the bimetallic catalysts at higher pressures (above 100 Torr), especially for the better dispersed 2.2% Cu–0.78% Pt/SiO_2 sample, produced coverages too high to be attributed only to Pt_s sites, thus indicating H spillover to the "Cu_2O" surfaces. The parallel H_2 isotherms for total and reversible adsorption after reduction at 473 K (see Fig. 2) supports this conclusion, as there is little or no reducible Cu^{+1} remaining in the catalyst. Although extrapolation through the inflection point to zero pressure to correct for adsorption on the support gives an uptake that is quite consistent with that expected for only Pt_s sites, this inflection is not always well defined, as revealed in Fig. 4. However, H spillover is an activated process; consequently, by conducting the H_2 titration reaction at a low enough temperature, this transport process can be inhibited. While the H_2 titration reaction occurs readily near 210 K (45), this temperature should be low enough to inhibit H spillover, and the results in Table 4 for both bimetallic catalysts validate this statement because the number of Pt_s atoms counted by this method are very consistent with those determined by the other adsorption measurements. Consequently, the chemistry represented by Eq. 2 can be used at 210 K to selectively count Pt_s atoms in Pt–Cu systems.

It has been previously established that the CO–N_2O titration reaction on a 0.81% Pt/SiO_2 catalyst at 300 K gave an irreversible CO coverage value equal to the hydrogen monolayer coverages obtained by either H_2 adsorption or the H_2–N_2O titration reaction (34, 35). Consequently, application of the CO–N_2O titration reaction to Pt–Cu bimetallic catalysts might be expected to enable counting of the total number of surface metal atoms ($Pt_s + Cu_s$) according to Eqs. [3] and [4],

$$Pt_s\text{–}O + 2CO_{(g)} \rightarrow Pt_s\text{–}CO + CO_{2(g)}, \qquad [3]$$

$$Cu_s^{+1} + CO \rightarrow Cu_s^{+1}\text{–}CO. \qquad [4]$$

In either case, the net volumetric gas uptake gives a CO_{ad}/M_s ratio of unity provided no significant CO_2 adsorption occurs, which is typically a valid assumption at these temperatures. Irreversible CO uptakes on the reduced bimetallic surfaces determined by both volumetric and gravimetric measurements were in good agreement, and the predicted net weight gains during CO adsorption on the O-covered bimetallic catalysts were consistent with the experimental values. The DRIFT spectrum of CO chemisorbed on the reduced surface of the 3.4% Cu–0.78% Pt–SiO_2 catalyst exhibits only a band at 2061 cm^{-1} representing a linear CO species adsorbed on Pt_s, whereas the spectrum for CO on an O-covered surface via dissociative N_2O adsorption at 363 K reveals two bands, i.e., one at 2121 cm^{-1}, which is indicative of CO adsorbed on Cu_s^{+1} sites (36) and the other for CO on reduced Pt_s atoms, as expected if Eqs. [3] and [4] are correct. The reduced sample, which should have only Cu_s^0 atoms, exhibited no IR bands indicative of CO adsorbed on any Cu_s species, as anticipated because CO adsorption on metallic Cu_s atoms is weak and reversible at 300 K. The IR spectrum for CO adsorption on the O-covered Cu–Pt surface is similar to spectra reported recently for well-dispersed Cu–Pt clusters which were assumed to be fully reduced, without verification; thus the authors attributed the 2125-cm^{-1} band to reduced Cu_s^0 atoms present in bimetallic clusters (66).

After reduction at 673 K, the 0.78% Pt/SiO_2 catalyst had a H/Pt_{tot} value of 0.58, which corresponds to a crystallite size of 2.0 nm using the relationship of $d_p\ (\text{nm}) = 1.13/(H/Pt_{tot})$ (48), which would result in diffraction peaks that are too broad to be observed easily by XRD. However, when the two Cu–Pt catalysts were reduced at 573 K, XRD peaks for Pt were readily visible, indicating that Pt agglomerates during the procedure used to impregnate the Cu salt and subsequently reduce it. No bulk alloy phase was formed, however, because no appreciable shift in the angular position of their diffraction lines occurred (1, 21). The Pt crystallite sizes indicated by XRD line broadening were 7.1 and 13 nm for the bimetallic 2.2% and 3.4% Cu catalysts, respectively, comparable to, but smaller than, the sizes based on the results from the different adsorption methods. These results imply a particle system with Pt cores partially covered by Cu atoms, as expected from the preparative procedure. The inconsistency in the Cu sizes in these bimetallic catalysts based on adsorption vs XRD methods could be due to an unknown amount of nonreducible Cu in the catalyst, which would prevent meaningful calculations for metallic Cu dispersions. However, overoxidation of the Cu during air exposure following the passivation step is perhaps more likely to contribute to this discrepancy, especially with Pt present to dissociate O_2, and additional oxidation in air would produce an eggshell phase of "Cu_sO" and/or CuO surrounding a metallic Cu core, which would decrease the size of the Cu^0 crystallites but would not be easily observable in XRD patterns if it were thin enough. The higher N_2O exposure temperature of 393 K gives better agreement with the XRD results, but the reason for this is not known at this time.

The results of this study provide strong evidence that Cu^{+1} species do not exist at the surface of the 2.2% Cu–0.78% Pt/SiO_2 catalyst after using pretreatment I (LTR573) and that H atoms on Pt_s near 200 K do not migrate onto Cu_2O surfaces. Based on these assumptions, the following model can be proposed. If all the irreversible CO adsorption on the reduced catalyst is associated with surface Pt atoms, which is consistent with the DRIFT spectra which showed no Cu^{+1}–CO band, then the 5.0 μmol of CO_{irr}/g corresponds to 5.0 μmol of Pt_s/g. The value of 4.1 μmol of Pt_s/g based on the H_2–N_2O titration reaction conducted at 200 K gives a value close to that for CO_{irr}. If the H_2 titration uptake at low pressure before the inflection point, around 100–150 Torr, is associated only with O atoms on Pt_s, then an average Pt_s value of 4.8 μmol/g is obtained from the three titration reaction measurements conducted in three different H_2 pressure ranges, which is also consistent with this model. If all three approaches are considered, an average value of 4.7 μmol of Pt_s/g is attained, which is close to the average value based only on CO_{irr} and H_2–N_2O titration at 200 K. The total amount of surface metal atoms ($Pt_s + Cu_s^{+1}$) is 8.5 μmol/g from the volumetric CO–N_2O reaction; thus 3.8 μmol of Cu_s^{+1}/g exists if the average value for Pt_s is used for this catalyst. The predicted O uptake via N_2O decomposition would be $4.7/2 + 3.8/4 = 3.3$ μmol of O_2/g or 6.6 μmol of O/g on the reduced catalyst, assuming $O/Pt_s = 1$ and $O/Cu_s^0 = 1/2$, which is consistent with the gravimetric O_{irr} uptake of 6.8 μmol/g. The consistency between the volumetric and gravimetric measurements of CO uptake should be noted. The additional H_2 uptake at higher pressures (and longer times) can be attributed to migration of H atoms from Pt_s sites to the "Cu_2O" phase, and estimates based on these amounts, represented by the difference between the total uptake at "high" pressure (line L_I) and that near 150 Torr (line $L_{I'}$), give an average value near 10.7 μmol of H/g. If it is assumed that all this hydrogen interacts with the Cu^{+1} surface phase via spillover according to the reaction

$$Cu_s\text{–}O\text{–}Cu_s + 2H_{(spill)} \rightarrow 2Cu_s^0 + H_2O_{(ad)}, \qquad [5]$$

then the amount of Cu_s present is similar to that noted in Table 4. This model is also applicable to the bimetallic 3.4% Cu–0.78% Pt/SiO_2 catalyst, which has around 3.6 μmol of Pt_s/g and 4.8 μmol of Cu_s/g based on the volumetric CO–N_2O titration value of 8.4 μmol of CO_{irr}/g. The CO_{irr} uptake on the reduced sample is the same as the Pt_s value determined by the H_2–N_2O titration reaction conducted at 200 K, whereas the value from the latter reaction conducted at 300 K and determined via the inflection point is somewhat higher. Based on these two concentrations of Pt_s and Cu_s, an irreversible oxygen uptake of 6.0 μmol of O/g is predicted, which is in excellent agreement with the experimental value of 6.1. Again, the CO uptakes determined volumetrically and gravimetrically are in good agreement.

SUMMARY

Significant irreversible hydrogen adsorption occurred at 300 K on Cu^0 atoms in a 1.96% Cu/SiO_2 catalyst but no adsorption was measured on a Cu_s–O–Cu_s monolayer surface created by dissociative N_2O adsorption on Cu^0 surfaces at 363 K. However, CO molecules are irreversibly adsorbed at 300 K on Cu^{+1} sites; thus the combination of N_2O decomposition and CO adsorption offers a volumetric approach not only to count the total number of Cu_s atoms, but also to distinguish between Cu_s^0 and Cu_s^{+1} sites. The use of the H_2–N_2O titration reaction following O chemisorption via N_2O decomposition at 363 K allows one to count only Pt_s atoms in a bimetallic Cu–Pt system if the reaction is performed at a low temperature, such as 200 K, in order to eliminate H spillover. When conducted at 300 K, this latter phenomenon creates a problem which, however, can sometimes be corrected for by the appearance of an inflection point in the titration isotherm. On a fully reduced Cu–Pt catalyst, irreversible CO chemisorption occurs only on Pt_s sites, which provides another means of determining Pt_s atoms. The CO–N_2O titration reaction can be used in this system to count the total number of surface metal atoms ($Pt_s + Cu_s$); therefore, combining this measurement with H_2–N_2O titration and CO adsorption on the reduced sample provides a method to determine overall (total) metal dispersion as well as surface composition. Exposure of a reduced bimetallic catalyst to CO at 300 K gave a single band at 2061 cm^{-1} due only to linearly adsorbed CO on surface Pt_s atoms, while an oxidized surface via dissociative N_2O adsorption exhibited a substantial 2121-cm^{-1} band indicative of CO coordinated on Cu^{+1} sites, as well as the 2060-cm^{-1} peak for CO on Pt_s. The model used to describe the adsorption behavior of this Cu–Pt system was consistent with these DRIFTS results. Consequently, the combination of these techniques can be used to characterize the surface in bimetallic Cu–Pt systems, and this approach may be applicable to other bimetallic Group VIII–Group IB combinations.

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