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Dissociative N_2O Adsorption on Supported Pt

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The oxygen monolayer coverage obtained by N_2O adsorption/decomposition at 363 K on a 0.81% Pt/SiO_2 catalyst was compared to those acquired by H_2, O_2, and CO chemisorption. It was equal to the hydrogen monolayer coverage, but about 8% higher than the O coverage acquired by dissociative O_2 chemisorption at either 300 or 363 K, and about 20% greater than irreversible CO coverage. Titration of the O-covered Pt surface obtained via N_2O decomposition gave a dispersion value in excellent agreement with that based on H chemisorption, whereas the dispersion value based on titration of an oxygen monolayer obtained by dissociative O_2 chemisorption was slightly lower, as expected. Thus the appropriate stoichiometry for N_2O adsorption is $Pt_s + N_2O_{(g)} \rightarrow Pt_s - O + N_{2(g)}$. Diffuse reflectance IR Fourier transform (DRIFT) spectra of CO chemisorbed on either clean or O-covered SiO_2-supported Pt surfaces gave one predominant peak at 2073 ± 3 cm^{-1} for linearly adsorbed CO and indicated a small extent of bridge-bonded CO. CO adsorption on an O-covered surface also gave a band at 2188 cm^{-1}, indicative of a small residual amount of oxidized Pt; however, H_2 titration completely removed all surface oxygen. The CO adsorption process is adequately described by $Pt_s - O + 2CO_{(g)} \rightarrow Pt_s - CO + CO_{2(g)}$. Similar measurements with a commercial 3% Pt/C catalyst revealed that a large, irreversible O_2 uptake occurred on the carbon surface at either 300 or 363 K; however, the amount of titratable oxygen at 300 K was similar to, but slightly higher than, the amount of chemisorbed hydrogen. The oxygen coverage established by N_2O decomposition was titrated and found to be slightly lower than the H coverage. DRIFT spectra of CO adsorbed on the Pt/C catalyst gave a single band whose maximum varied from 2019 to 2047 cm^{-1}, depending on the pretreatment. © 2001 Elsevier Science

INTRODUCTION

Supported precious metals are widely used to catalyze industrial petroleum and chemical reactions. A fundamental concern in metal-catalyzed reactions is the relationship between catalytic activity and the dispersion of the metal (i.e., the crystallite size) in supported catalysts; consequently, the number of surface metal atoms needs to be determined to provide an answer to this important question. The most sensitive and reliable methods for obtaining the dispersion (fraction exposed) of metals involve the selective chemisorption of probe molecules, such as H_2, CO, and O_2, in which these gases are strongly chemisorbed on the metal surface but not on the support (1). Another adsorption technique is the titration of an adsorbed species using another gas molecule, as in the case of the titration of chemisorbed oxygen by H_2, which was first established with Pt and can increase sensitivity and decrease effects due to contamination (2, 3). It is well-known that H_2 is dissociatively chemisorbed on noble metals, such as Pt, Pd, Ir, and Rh, but a precise adsorption stoichiometry on surface metal atoms, M_s, around 300 K is less well established although H/M_s ratios near unity are routinely utilized (2–5). However, there is some uncertainty whether this ratio is most applicable to the total H coverage under a H_2 pressure or to the irreversibly adsorbed H remaining after evacuation at 300 K and, for example, H/Pt_s ratios approaching 2 have been reported for the former coverage on highly dispersed Pt (6–8). The adsorption stoichiometry for CO can be dependent on the crystal planes present, crystallite size, and mode of adsorption (linear vs bridged) (1, 4, 9), while the stoichiometry for adsorbed oxygen has been reported to be lower than that for hydrogen and near an O/Pt_s value of 0.5 on very small Pt crystallites (6).

The determination of surface stoichiometries for oxygen on metal surfaces after chemisorption of O_2 can be complicated by incomplete monolayer formation during immobile dissociative adsorption as well as by bulk oxidation, as with Cu. An additional problem exists if O_2 can react with or adsorb on the support being used. One approach to alleviate those difficulties is the chemisorption of O atoms via the dissociative adsorption of N_2O under specified conditions, as first employed by Stone and co-workers to characterize metallic Cu surfaces according to the following reaction (10):

$$2Cu_s + N_2O_{(g)} \rightarrow Cu_s - O - Cu_s + N_{2(g)}. \qquad [1]$$

Scholten and Konvalinka subsequently provided early additional support that only one monolayer of Cu_2O is formed

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at temperatures near 373 K (11), and Narita *et al.* later added verification of this (12); consequently, numerous groups employing a variety of experimental techniques have used this reaction to characterize Cu catalysts [11–21]. More recently, N_2O decomposition to leave chemisorbed oxygen atoms has also been applied to Ag [22, 23] and Ru [24] surfaces; however, the adsorption stoichiometries differ from that in reaction [1]. Ultrahigh vacuum (UHV) studies of N_2O on single crystals of Cu, Ni, Pt, Rh, Ru, and W have been conducted (25–31), and N_2O was found to adsorb very weakly on Cu, Ni, and Pt at low temperatures (25–27). At higher temperatures, dissociative N_2O adsorption occurred on Re and Rh filaments (32, 33), but Avery found no N_2O dissociation on Pt(111) (27).

Although N_2O decomposition kinetics have been examined on Pt filaments and wires (34–36), we could find no studies of N_2O adsorption on Pt at higher temperatures and pressures; thus the adsorption stoichiometry for oxygen on Pt via this reaction is not known. Therefore, this study was conducted to measure O coverages established by N_2O decomposition and to compare them with those established by O_2, H_2, and CO chemisorption. This knowledge could lead to other ways to determine Pt dispersion (i.e., by O chemisorption via N_2O dissociation and/or its subsequent titration with H_2) once the stoichiometry is known for the following reaction:

$$\mathrm{Pt_s} + x\mathrm{N_2O_{(g)}} \rightarrow \mathrm{Pt_s} - \mathrm{O}_x + x\mathrm{N_{2(g)}}. \qquad [2]$$

EXPERIMENTAL

Catalyst Preparation

SiO_2 having a surface area of 220 m^2/g (Davison 57) was ground and sieved to a 60/80 mesh particle size to prepare a supported Pt catalyst. Before loading the Pt onto the SiO_2, it was calcined at 773 K for 4 h in flowing O_2 (MG Ind., 99.999%) at 1.5 L/min. Pt/SiO_2 containing 0.81% Pt was obtained by an ion exchange method using the following procedure (37, 38): (a) use distilled, deionized water to prepare a NH_4OH solution with a pH of 9.8; (b) add the calcined SiO_2 to the aqueous solution with rigorous stirring; (c) slowly add dropwise an aqueous solution of $Pt(NH_3)_4Cl_2$ (Aldrich, 99.995%); (d) monitor the pH of the solution–solid mixture; (e) add five to six drops of concentrated NH_4OH solution into the mixture to compensate for the pH decrease after about 2 h; (f) maintain the mixture with constant stirring overnight; (g) filter and wash the resulting catalyst with distilled deionized water; and (h) dry the catalyst at 393 K in air overnight. The dried catalyst was stored in a desiccator for later use. The 3% Pt/C was received from Monsanto Company and was prepared by the wet impregnation of a Westvaco SA30 carbon.

Volumetric Adsorption Measurements

A stainless steel high-vacuum system giving a dynamic vacuum below 10^{-7} Torr (1 Torr = 133.3 Pa) was used for the adsorption of probe molecules on supported Pt catalysts. The system was equipped with a Balzers Type TPU 170 turbomolecular pump (Pfeiffer Vacuum Technologies) backed by an Edwards Model RV12 mechanical pump to obtain a high dynamic vacuum, which was monitored by a Granville–Phillips Model 260 gauge controller. Changes in gas pressure during the volumetric adsorption measurements of N_2O, H_2, CO, and O_2 were detected using a differential pressure gauge (Type 270B, MKS Instruments) connected to a Baratron Type 310CA pressure sensor, while temperature was monitored by an Omega Model 412B-J Digicator. Details of such an adsorption system have been given elsewhere (21, 39). All catalysts were pretreated *in situ* in a laboratory-designed chemisorption cell placed in a cylindrical electric furnace with a PID temperature controller (Omega, Model CN20110) using one of the two pretreatment protocols described in Table 1. In this study, reduction at 673 K is designated HTR (high-temperature reduction) to distinguish it from a low-temperature reduction (LTR) at 473 K used in another part of this program. All gas flow rates during the pretreatment were maintained at 32 cm^3/min using Tylan Model FC 260 mass flow controllers. Prior to introducing the probe gas into the adsorption system, the H_2, O_2 (MG Industries, 99.999%) and CO (Matheson, 99.99%) were purified by flowing them through Drierite and molecular sieve 5A traps (Alltech Associates). Both H_2 and CO were further purified using commercial Oxytraps (Alltech Associates). Argon (MG Industries, 99.999%), used for both catalyst pretreatment and dead-volume calibration, was purified in a way similar to that for H_2 and CO. Only moisture traps similar to the two described above were used for N_2O (BOC, medical grade, 99.9%).

TABLE 1

Pretreatments for Supported Pt Catalysts

Pretreatment I (HTR)
1. Heat to 673 K and hold for 1 h in flowing He (760 Torr).
2. Reduce in flowing H_2 (760 Torr) for 1 h at 673 K.
3. Cool to 648 K in H_2.
4. Evacuate at 648 K for 30 min.
5. Cool to 300 K and continue evacuation for 1 h at 300 K.

Pretreatment II (HTR)
1. Reheat to 648 K and hold for 15 min in flowing H_2 after using pretreatment I (HTR).
2. Evacuate at 648 K for 30 min.[a]
3. Cool to 363 K in vacuum.
4. Expose to 10% N_2O (76 Torr) 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 at 300 K.

[a] Establishes conditions after step 3 of pretreatment I (HTR).

The 0.81% Pt/SiO_2 was routinely reduced using pretreatment I (HTR), and first the hydrogen adsorption at 300 K was measured at pressures ranging from 40 to 350 Torr. The titration of O atoms deposited on the Pt surface via N_2O decomposition at 363 K was of particular interest, and this reaction is designed H_2–N_2O titration. Both total and reversible uptakes for H_2 adsorption and the H_2 titration reaction on silica-supported Pt were determined by extrapolating the linear regions of the isotherms (typically from 150 to 350 Torr), corresponding to saturation coverage on the Pt, to zero pressure to correct for adsorption on the support, as described elsewhere (2, 5). After the initial reduction using pretreatment I (HTR), all other adsorption measurements (i.e., CO and O_2 chemisorption at either 363 or 300 K) were also preceded by pretreatment I (HTR). After adsorbing O_2 at either 363 or 300 K, the O monolayer was titrated with H_2 via the standard titration reaction (designated H_2–O_2 titration) to allow comparison with the H_2–N_2O titration reaction. The dual isotherm technique used by Yates and Sinfelt was employed to determine the CO irreversibly adsorbed on the Pt surface at 300 K (40). In addition to these consecutive chemisorption and titration experiments with N_2O, H_2, O_2, and CO on a single sample, each uptake was also measured on a different sample to verify that the Pt particle size was not altered by the repeated use of one sample. Volumetric measurements were conducted with the same probe gases with the 3% Pt/C catalyst in a similar fashion.

Gravimetric Adsorption Measurements

Gravimetric measurements of the adsorption of "O" atoms via N_2O decomposition at 363 K on these Pt catalysts were conducted using a Perkin–Elmer TGS-2 thermogravimetric system with an instrumental sensitivity of 0.1 μg, as described earlier (21). An appropriate amount of the catalyst (ca. 7–9 mg) was loaded into the sample holding pan and reduced *in situ* at 673 K for 1 h in a mixture of 30% H_2 in Ar flowing at a rate of 60 cm^3/min according to pretreatment I (HTR), but with evacuation replaced by pure flowing Ar. After cooling to 363 K, the online weight suppression unit was employed to obtain higher sensitivity during the weight-gain measurement. The catalyst was exposed to a flowing mixture of 10% N_2O/90% Ar for 30 min at 363 K to deposit oxygen atoms on the Pt, then this feed gas stream was switched to a flow of pure Ar to remove N_2O reversibly adsorbed on the catalyst. The net weight gain due to oxygen chemisorption on Pt was determined by subtracting the initial weight from the final one. All gases used were purified in a fashion similar to that described previously; however, Ar as both a carrier gas and a system purge gas was specially cleaned to an impurity level less than 1 ppb by passing it through an Aeronex GateKeeper purifier (Model 400 K, Supelco).

Infrared Spectroscopic Measurements

In situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) studies were conducted using a Mattson Research Series 10000 spectrometer coupled with a Harrick Scientific DRA diffuse reflection cell with NaCl windows. A feed gas handling system and temperature controller were combined with this infrared system to allow *in situ* sample pretreatments. Details for this DRIFTS system have been provided elsewhere (41, 42). The catalyst sample (ca. 100 mg) was loaded into the infrared cell and subjected to one of the pretreatment procedures described in Table 1. The sample was first given pretreatment I (HTR) and scanned at 300 K to obtain an interferogram which was used as a background for Fourier transforming the sample spectra. Following this, a gas mixture of 10% CO/90% He was flowed through the cell for 30 min at 300 K, a second interferogram was taken in the presence of CO, and then a final spectrum was collected after purging the IR cell with pure He for 30 min. Similar spectra-collecting protocols were used with the catalyst after either O_2 adsorption at 76 Torr and either 300 or 363 K (following pretreatment I (HTR)) or N_2O decomposition at 363 K and 76 Torr (after pretreatment II (HTR)). Spectra of CO adsorbed at 300 K on either of these oxidized surfaces were compared with spectra of CO adsorbed on these surfaces following the H_2 titration reaction at 300 K under flow conditions (335 Torr H_2 in a He flow). Oxygen chemisorption at 300 K on the HTR catalyst was also conducted. Each interferogram in the presence and absence of CO at 300 K was Fourier transformed using a background which had been collected prior to introducing the CO. All interferograms were recorded with a resolution of 4 cm^{-1} and a scan number of 1000. A spectrum of gas-phase CO, taken in the DRIFTS cell using an aluminum mirror, was subtracted from each spectrum obtained under CO pressure. Pretreatment procedures for each experiment in the DRIFTS system were basically identical to those for the volumetric system. All gases were purified in a way similar to that described previously and controlled at a total flow rate of 20 cm^3/min.

RESULTS

To allow adsorptive decomposition of N_2O at 363 K on 0.81% Pt/SiO_2, the sample underwent pretreatment II (HTR) and then, after evacuating and cooling to 300 K, the hydrogen titration reaction (H_2–N_2O titration) was conducted to determine the extent of coverage of the Pt surface by chemisorbed oxygen. These values were around 37.5 μmol H_2/g and were very reproducible, as shown in Table 2. The regular H_2 titration values for oxygen chemisorbed at 300 K (H_2–O_2 titration) are also given, along with those after O_2 chemisorption at 363 K. The total hydrogen uptake on this catalyst was 12.7 μmol H_2/g, with the irreversible amount being half of this (6.3 μmol H_2/g).

TABLE 2

Adsorption of N_2O at 363 K and H_2, O_2, and CO at 300 K on 0.81% Pt/SiO_2

		Gas uptake (μmol/g)						Dispersion based on[b]					
Sample	Pretreatment	H_2–N_2O titr	H_2 Tot	O_2 Irr	CO Irr	H_2–O_2 titr	"O"[a]	$\frac{H_{titr}–N_2O}{Pt}$	$\frac{H_{tot}}{Pt}$	$\frac{O_{irr}}{Pt}$	$\frac{CO_{irr}}{Pt}$	$\frac{\text{"O"}}{Pt}$	$\frac{H_{titr}–O_2}{Pt}$
A	II (HTR)	37.3 ± 0.1						0.60					
	I (HTR)		12.7 ± 0.1	11.3 ± 0.1	18.6 ± 0.2	34.5 ± 0.2	24.2[c]		0.61	0.55	0.45	0.58	0.55
				11.4 ± 0.1[c]		34.1 ± 0[d]				0.55[c]			0.55[d]
B	II (HTR)	37.7						0.60					
C	I (HTR)		12.7 ± 0.1						0.61				
D	I (HTR)			11.6						0.56			
E	I (HTR)			11.4						0.55			
F	I (HTR)			11.3[c]						0.54			
G	I (HTR)				18.3						0.44		
E	I (HTR)					34.2							0.55
F	I (HTR)					34.2[d]							0.55[d]

Note. No irreversible CO adsorption on pure SiO_2 after any pretreatment.

[a] Atomic O via N_2O decomposition at 363 K measured gravimetrically.

[b] Assuming $H/Pt_s = O/Pt_s = CO/Pt_s = 1$.

[c] At 363 K.

[d] H_2 titration at 300 K after exposure to O_2 at 363 K.

All oxygen adsorption on the Pt was irreversible, as shown by the reversible adsorption isotherm extrapolated to zero pressure, whether at 300 or 363 K, and both uptakes were essentially the same. The irreversible CO uptake at 300 K is also listed in Table 2. It is clear that uptake values were very reproducible among the different samples, and repeated pretreatments and measurements on a single sample did not alter values. A typical set of isotherms is shown in Fig. 1.

To independently determine the extent of oxygen chemisorption via N_2O decomposition at 363 K, this reaction was also conducted in the gravimetric system after a sample of 0.81% Pt/SiO_2 had been given pretreatment II (HTR). An appreciable weight change was recorded after the introduction of 10% N_2O (76 Torr) in flowing Ar, as shown in Fig. 2, and a net weight gain of 3.0 μg was recorded for oxygen chemisorbed on the Pt surface, which corresponds to an "O" uptake of 24.2 μmol/g. CO adsorption on pure SiO_2 obeyed Henry's law, passed through zero at $P = 0$, and was negligible, with a maximum uptake of less than 1 μmol/g at 300 Torr. Finally, X-ray diffraction (XRD) measurements yielded no discernable Pt peaks, even after subtraction of the silica background.

To extend the N_2O adsorption method to an industrial catalyst, the 3% Pt/C catalyst obtained from Monsanto was subjected to a similar study, and the results are listed in Table 3. The two significant differences are the absence of a gravimetric "O" uptake and an additional N_2O exposure at 300 K to determine the influence of temperature on N_2O decomposition to give chemisorbed oxygen. This system was complicated by very large irreversible oxygen uptakes that occurred at either temperature when exposed to O_2, which were undoubtedly associated with the carbon surface; however, this complication did not exist with oxygen adsorption via N_2O decomposition and indicates one of the benefits of the latter approach. XRD results with this Pt/C catalyst indicated a very broad line around $2\theta = 39.8°$, which, when corrected for the carbon support background,

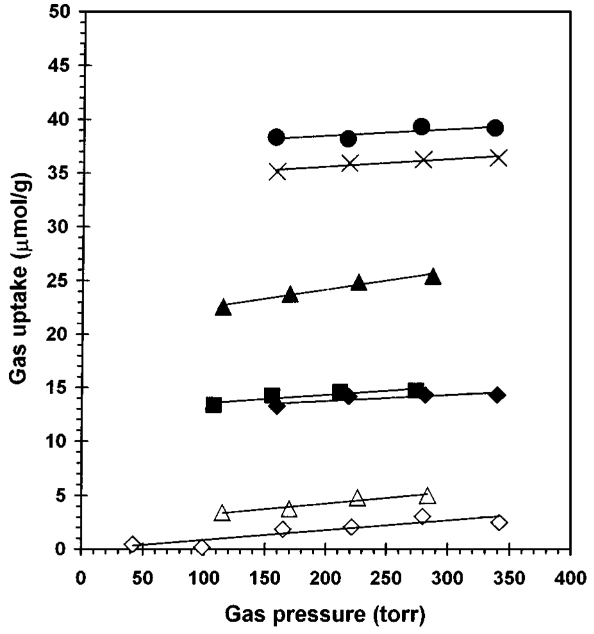

FIG. 1. Adsorption isotherms on 0.81% Pt/SiO_2 after either pretreatment II (HTR) or I (HTR). (●) H_2 titration–N_2O; (■) H_2 adsorption; (▲, △) CO adsorption; (◆, ◇) O_2 adsorption; (×) H_2 titration–O_2. Open and closed symbols present the respective total and reversible gas uptakes at 300 K.

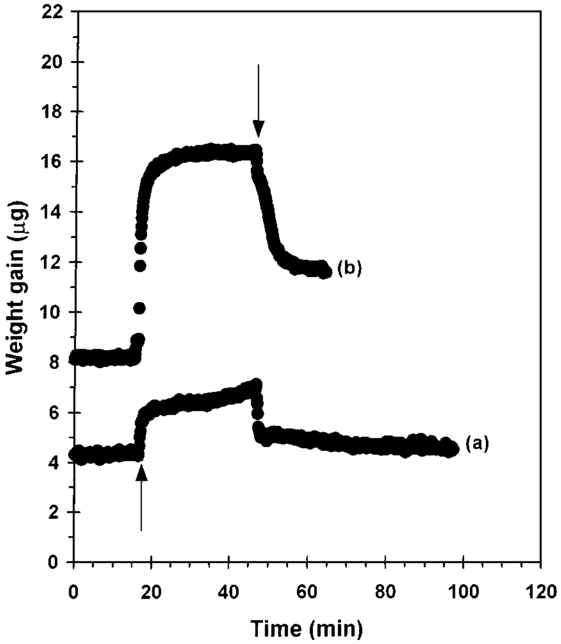

FIG. 2. Gravimetric measurement for N_2O decomposition at 363 K on (a) pure SiO_2 and (b) 0.81% Pt/SiO_2 following reduction at 673 K. In each case the lower arrow indicates when N_2O was admitted and the upper arrow indicates when the Ar purge began.

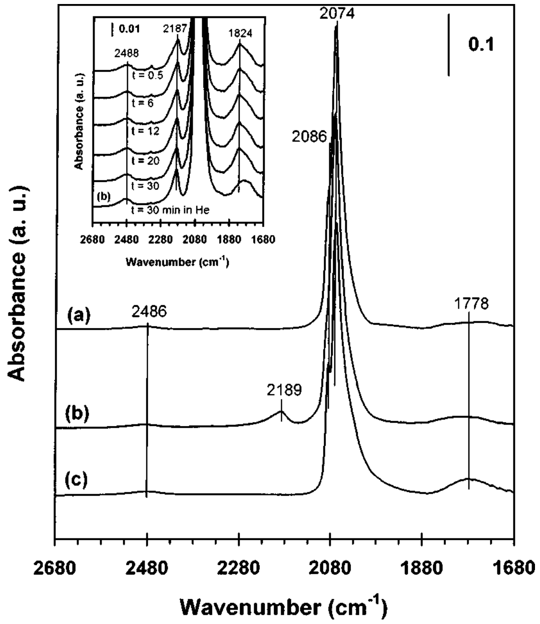

FIG. 3. DRIFT spectra of CO adsorbed at 300 K on 0.81% Pt/SiO_2 after different pretreatments (see Table 1) and a He purge: (a) after pretreatment I (HTR); (b) after pretreatment II (HTR); (c) after pretreatment II (HTR) followed by H_2 titration at 300 K under flowing 45% H_2 in He. (Inset) Spectra taken as a function of exposure time to CO after pretreatment II (HTR).

gave a Pt crystallite size near 2.5 nm, indicating a dispersion of 0.45, a value consistent with those obtained from the H_2 chemisorption and titration techniques. However, if only linearly adsorbed CO is assumed to exist, dispersions based on irreversible CO uptakes are again consistently lower.

DRIFT spectra of CO adsorbed on 0.81% Pt/SiO_2 following different pretreatments are provided in Figs. 3 and 4. The adsorption of CO at 300 K on an O-covered surface was of particular interest because of the need to ascertain the extent of oxygen removal via CO_2. CO adsorption on a clean Pt surface after reduction of 673 K gave, after purging, a very strong peak at 2074 cm^{-1}, with a shoulder at 2086 cm^{-1} and a very weak band near 1778 cm^{-1}, as shown in Fig. 3a. No peaks were detected with pure SiO_2. Spectra taken after CO adsorption on a catalyst surface covered by "O" atoms via N_2O decomposition at 363 K are shown as a function of exposure time in the inset of Fig. 3, and the final spectrum after purging is given in Fig. 3b. As indicated in the inset, after 30 s in flowing CO at 300 K, peaks at 2488, 2340, 2187,

TABLE 3

Adsorption of N_2O at 363 K and H_2, O_2, and CO at 300 K on 3% Pt/C

Sample	Pretreatment	Gas uptake (μmol/g)					Dispersion based on[a]				
		H_2–N_2O titr	H_2 Tot	O_2 Irr	CO Irr	H_2–O_2 titr	$\frac{H_{titr}-N_2O}{Pt}$	$\frac{H_{tot}}{Pt}$	$\frac{O_{irr}}{Pt}$	$\frac{CO_{irr}}{Pt}$	$\frac{H_{titr}-O_2}{Pt}$
A	II (HTR)	86.3 ± 0.2					0.37				
B	I (HTR)		30.9 ± 0.9	193.5 ± 0.5[b]	35.5	102.7 ± 0.7		0.40	(2.51)[b]	0.23	0.44
				329.5[b,c]		113.9[d]			(4.28)[b,c]		0.49
C	I (HTR)		33.3					0.43			
D	I (HTR)			191.1[b]					(2.48)[b]		
E	I (HTR)				35.5 ± 0.7					0.23	
F	I (HTR)	58.9[e]					(0.25)[e]				

[a] Assuming $H/Pt_s = O/Pt_s = CO/Pt_s = 1$.

[b] Not corrected for irreversible oxygen uptake on the pure carbon (27.5 μmol O_2/g at 300 K).

[c] At 363 K.

[d] H_2 titration at 300 K after exposure to O_2 at 363 K.

[e] H_2 titration at 300 K after exposure to N_2O for 30 min at 300 K.

and 1824 cm^{-1} were visible along with a predominant peak at 2078 cm^{-1} with a very weak shoulder at 2091 cm^{-1}. All peaks were unchanged in their position and intensity after a 30-min exposure, except for the 2340 cm^{-1} peak, which decreased with time, and a purge with pure He at 300 K left all bands except that at 2340 cm^{-1}. When the catalyst was exposed to N_2O at 363 K, titrated with a flow of 45% H_2/55% He at 300 K, then exposed to 10% CO (76 Torr) in flowing He, bands at 2482, 2086, 2070, and 1778 cm^{-1} were observed after purging, as seen in Fig. 3c. In these spectra, the peaks around 2070–2085 cm^{-1} represent linearly adsorbed CO on metallic Pt_s atoms with different coordination numbers while the bands around 1800 cm^{-1} and below represent multicoordinated (bridge-bonded) CO on Pt_s^0 sites (43–49). The peak near 2486 cm^{-1} is assigned to a combination mode of C–O and Pt^0–C symmetric stretching vibrations in on-top Pt^0–CO species (50). The 2340 cm^{-1} peak is the antisymmetric stretching mode of molecularly adsorbed CO_2 on silica (51, 52), and the 2189 cm^{-1} band represents CO adsorbed on oxidized surface Pt sites (53).

Figure 4 shows IR spectra of CO adsorbed on 0.81% Pt/SiO_2 after the catalyst surface was modified not only by exposing the reduced sample to 10% O_2 (76 Torr) in flowing He at either 363 or 300 K, but also by titrating the oxygen-covered surface at 363 K with flowing 45% H_2 in He at 300 K. After exposure to 10% CO in flowing He for 30 min followed by a He purge, the surface covered by chemisorbed oxygen at 300 K gave an intense absorption peak at 2074 cm^{-1}, along with a shoulder at 2087 cm^{-1} and three broad weak peaks at 2482, 2188, and 1782 cm^{-1}, as displayed in Fig. 4a. In a separate experiment, when an O-covered catalyst which had been prepared using O_2 adsorption at 300 K in a separate experiment was exposed to a flow of 10% CO in He at 300 K as a function of exposure time, it gave a peak at 2340 cm^{-1} whose band intensity decreased with time, and the band disappeared after a 30-min exposure followed by a 30-min purge with He at 300 K. When O_2 chemisorption was conducted at 363 K prior to CO adsorption at 300 K, peaks at 2481, 2359, 2340, 2184, 2080, and 1824 cm^{-1} could be observed in spectra obtained at different exposure times, as indicated in the inset to Fig. 4. As exposure time increased, the doublet at 2359 and 2340 cm^{-1} gradually decreased, the 2184 and 1824 cm^{-1} bands did not vary, and the 2184 cm^{-1} band shifted to a slightly higher frequency of 2188 cm^{-1} with increased intensity. The spectrum after a 30-min purge in pure flowing He at 300 K is shown in Fig. 4b. Similar time-dependent IR results were obtained prior to the spectrum of Fig. 4a. The principal distinction between the spectra of Fig. 4a and 4b is that the 2188 cm^{-1} band was enhanced by adsorption at 363 K while the 2086 cm^{-1} band intensity was decreased. Figure 4c shows the spectrum for CO adsorbed on the Pt surface after H_2 titration of the oxygen chemisorbed at 363 K. After purging, CO bands at 2480, 2086, 2071, and 1784 cm^{-1} were observed, and the spectrum is very similar to the spectrum of Fig. 3c. This indicates that all chemisorbed oxygen can be removed, and H_2 titration using N_2O can successfully evaluate Pt dispersion (fraction exposed). In either case, the H-covered catalyst gave a more intense band near 1780 cm^{-1} for bridging CO on Pt_s, and no band near 2188 cm^{-1} was detected.

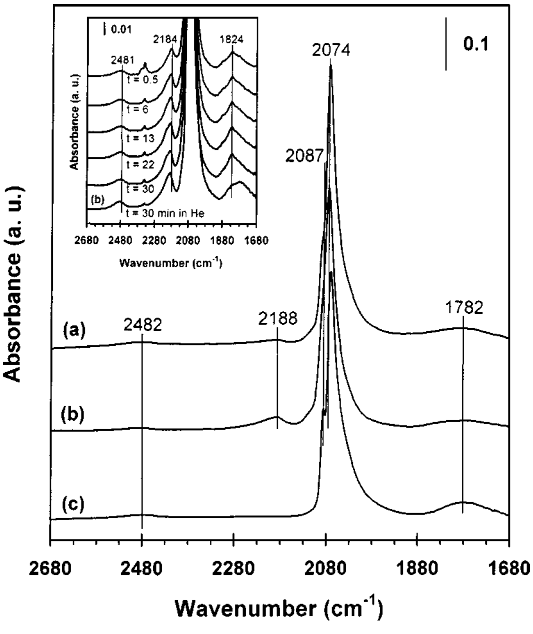

FIG. 4. DRIFT spectra of CO adsorbed on 0.81% Pt/SiO_2 after different pretreatments and a He purge: (a) after pretreatment I (HTR) followed by O_2 adsorption at 300 K; (b) after pretreatment I (HTR) followed by O_2 adsorption at 363 K; (c) after pretreatment I (HTR) followed by O_2 adsorption at 363 K, then H_2 titration at 300 K under flowing H_2 (45% in He). (Inset) Spectra taken as a function of exposure time to CO prior to spectrum (b).

A similar set of DRIFT spectra at 300 K were obtained with the 3% Pt/C sample. The spectrum of CO adsorbed after reduction at 673 K is shown in Fig. 5a, and the spectrum of CO adsorbed on a H-covered surface, obtained by cooling from 648 to 300 K under H_2 and then evacuating, is given in Fig. 5b. CO adsorbed on a reduced Pt surface following four O_2–H_2 titration cycles at 300 K is shown in Fig. 5c, while the spectrum for CO adsorbed on an O-covered surface after O_2 chemisorption at 300 K is given in Fig. 5d. After CO adsorption following reduction at 673 K and evacuation, one broad band between 1950 and 2060 was obtained (Fig. 5a). CO adsorbed on the Pt surface cooled in H_2 gave a narrower, stronger band with a maximum near 2035 cm^{-1} (Fig. 5b). Adsorption of CO on a reduced surface following four successive titration cycles at 300 K enhanced the intensity and shifted the band maximum to around 2045 cm^{-1} (Fig. 5c), and CO adsorbed on an O-covered surface

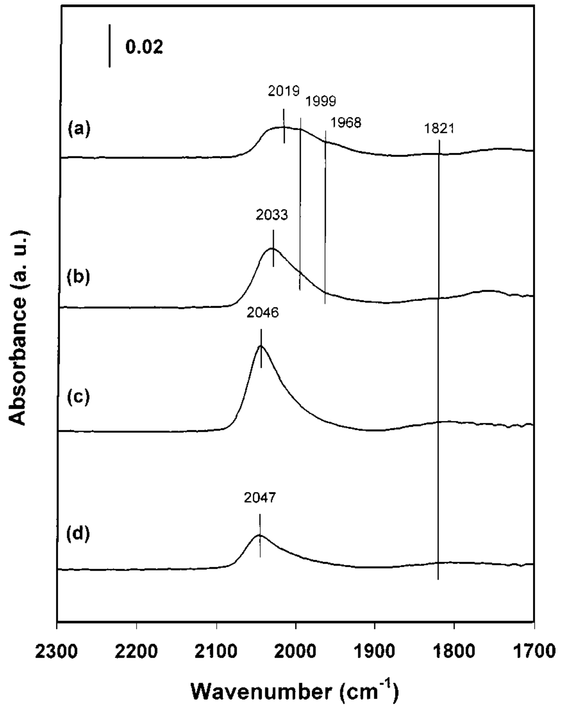

FIG. 5. DRIFT spectra of CO adsorbed on 3% Pt/C with each IR spectrum recorded after a 30-min purge with He at 300K: (a) directly after procedure I (HTR); (b) after cooling to 300 K in flowing H_2 and purging with He for 30 min; (c) after four H_2-O_2 titration cycles at 300 K and purging with He at 300 K for 60 min; (d) after O_2 chemisorption at 300 K for 30 min and purging with He at 300 K for 30 min.

provided a band similar to the latter one, but less intense (Fig. 5d). The spectrum of CO adsorbed on an O-covered carbon-supported Pt surface produced by exposure to N_2O at 363 K was essentially identical to that shown in Fig. 5d.

DISCUSSION

This paper is not intended to focus on the absolute stoichiometries of adsorption for hydrogen, oxygen, and carbon monoxide on Pt, but rather it is to examine the oxygen monolayer coverages obtained by N_2O decomposition and to compare them with coverages obtained by the chemisorption of H_2, O_2, and CO. Although saturated coverages of hydrogen on large, unsupported Pt particles routinely yield H_{ad}/Pt_s stoichiometries near unity (3, 54), ratios greater than one and sometimes approaching 2 have been reported for very small Pt crystallites dispersed on various supports (6–8, 54), and various explanations, such as metal–support interactions, hydrogen spillover, and low coordination metal sites, have been proposed to account for this. Near 300 K, both oxygen and CO monolayer coverages are consistently lower than that for hydrogen (54–56). Incomplete saturation coverage due to immobile adsorption (3) and/or a lower adsorption capacity on very small Pt crystallites and clusters (5) can decrease oxygen chemisorption via O_2 compared to hydrogen. Coverages of CO can depend on the crystal plane, and the occurrence of both linear and bridge-bond CO as well as surface reconstruction can further complicate the adsorption stoichiometry (57).

The uptakes on the Pt/SiO_2 catalyst studied here give very consistent results among themselves and with previous studies. The range of indicated dispersion, D, ca. 0.55–0.60, corresponds to crystallite sizes of 1.9–2.1 nm using the relationship $d(\mathrm{nm}) = 1.13/D$ (58), thus giving diffraction peaks too broad to be distinguished from the silica background by typical XRD spectra, which is consistent with our measurements. The O and CO coverages are lower than that for H atoms, with the O monolayer being equal, perhaps coincidentally, to that expected for an immobile monolayer with holes in it (92% saturation coverage) (3). One-half of the hydrogen coverage can be removed by evacuation at 300 K for 60 min, in agreement with previous studies of Pt dispersed on SiO_2 and Al_2O_3 (59, 60). If the total CO coverage via extrapolation to zero pressure (21.6 ± 1.0 μmol/g) is utilized, rather than the irreversible uptake, the coverage becomes almost equal to that for oxygen, in agreement with the results for the Pt/SiO_2 EUROPT-1 catalyst (55). Finally, the relatively equal amounts of O_{irr} at either 300 or 363 K and H_{tot} indicate that the titration equation originally proposed by Benson and Boudart (2),

$$\mathrm{Pt_s} - \mathrm{O} + 3/2\mathrm{H}_{2(g)} \rightarrow \mathrm{Pt_s} - \mathrm{H} + \mathrm{H_2O}_{(ad)}, \qquad [3]$$

is quite applicable here. This equation gives very consistent dispersions not only for O_2 chemisorbed at either 300 or 363 K, as expected, but also for the O monolayer formed by N_2O decomposition at 363 K. The latter coverage, whether determined gravimetrically or by H_2 titration, is consistently higher than the former by about 8% and is essentially equal to the hydrogen coverage. This could be due to the site pair requirement for immobile, dissociative O_2 adsorption, which does not exist for N_2O. Regardless, these results strongly imply that compared to O_2 adsorption, a slightly higher and essentially complete monolayer coverage of oxygen is established during N_2O decomposition at 363 K, and this oxygen is completely titrated by H_2 at 300 K. Consequently, despite the electron energy loss spectroscopy (EELS) results of N_2O adsorption on Pt(111) obtained by Avery (27), which revealed only weak adsorption and no evidence for decomposition under UHV conditions, and an earlier conclusion by Weinberg that N_2O decomposition on Pt is an improbable process (61), this reaction occurs readily to establish an apparently complete monolayer at 363 K and higher N_2O pressures. Thus, the most appropriate stoichiometry to describe the chemisorption of oxygen resulting from the decomposition of N_2O on

Pt appears to be

$$Pt_s + N_2O_{(g)} \rightarrow Pt_s - O + N_{2(g)}. \quad [4]$$

Thus, *x* in reaction [2] is unity.

Characterization of this catalyst by acquiring IR spectra of CO chemisorbed on both reduced and O-covered Pt surfaces was of interest to us because of the potential utilization of CO chemisorption to distinguish between surface atoms in bimetallic catalysts, such as Cu–Pt systems. A multitude of IR and EELS studies of CO on reduced Pt surfaces have been reported (43–50, 53, 56, 57, 62–72), and based on those earlier results, the CO absorption bands observed in this study (i.e., 2484 ± 4, 2188 ± 1, 2087 ± 1, 2073 ± 3, and 1786 ± 15 cm^{-1}) can be assigned. The weak 2484 cm^{-1} band is a combination mode of C–O and Pt–C stretching (50), the 2188 cm^{-1} peak is CO adsorbed on oxidized Pt (53, 66, 71), the 2087 and 2073 cm^{-1} bands indicate linearly adsorbed CO on Pt_s sites of different coordination number (e.g., 48, 49, 57), and the last band around 1786 corresponds to multiply coordinated (bridge-bonded) CO (57, and references therein). As stated earlier, the band near 2340 cm^{-1} was due to CO_2 created during reduction of the oxygen-covered Pt surface by CO.

The IR spectrum for CO on a clean reduced surface (Fig. 3a) is very similar to numerous previous spectra for CO on Pt/SiO_2, such as that for EUROPT-1 (56). Adsorption of CO at 300 K on an O-covered surface formed by N_2O decomposition provides a similar spectrum except that some Pt surface atoms are not completely reduced by CO at 300 K and a small peak for CO adsorbed on oxidized Pt_s sites is visible at 2189 cm^{-1}. This peak position has a higher wavenumber than that reported by Schwank and co-workers, but their Pt/SiO_2 catalyst was oxidized at 673 K for 90 min (66). However, titration of this surface at 300 K by H_2 completely removes all the surface oxygen, and the 2189 cm^{-1} peak disappears while there is a concomitant increase in the shoulder at 2086 cm^{-1}. The other noticeable difference between Fig. 3c and 3a is an enhancement in the amount of bridge-bonded CO. This could be due to the presence of a roughened Pt surface following titration. A similar pattern occurs when oxygen-covered Pt surfaces are created by dissociative O_2 chemisorption, as shown in Figs. 4a and 4b. Chemisorption of CO on the surface formed at 363 K again removes the oxygen, except for an amount comparable to that when N_2O was used; however, O_2 adsorption at 300 K results in a significantly smaller 2188 cm^{-1} peak (Fig. 4a). Titration of the former surface at 300 K by H_2 again removes all oxygen, increases the extent of bridge-bonding, and increases the 2087 cm^{-1} shoulder peak (Fig. 4c). Thus it seems that the oxidized Pt sites most difficult to reduce with CO at 300 K are converted by H_2 to Pt_s sites giving the latter CO peak. Regardless, this behavior coupled with the observation of CO_2 formation indicates that to a very good approximation, the chemisorption of CO at 300 K on an oxygen-covered Pt surface can be described as follows:

$$Pt_s - O + 2CO_{(g)} \rightarrow Pt_s - CO + CO_{2(g)}. \quad [5]$$

This stoichiometry has been verified by subsequent uptake measurements (73).

The results of this same approach when applied to a commercial Pt/C catalyst are given in Table 3. Two complications are quickly apparent. First and foremost, there is a great extent of interaction between O_2 and the support surface to give very large irreversible oxygen uptakes at 300 K, and this problem worsens at 363 K. In contrast, there was no reactivity between N_2O and the carbon support at 363 K, as no net weight change was detected. In addition, the CO uptakes are lower relative to those for hydrogen. The former problem prevents oxygen uptakes on the Pt surface from being determined directly; however, the reasonably close dispersion values based on H_2 uptakes and *titratable* oxygen, although they are somewhat higher (10–15%), indicate that the coverage of O atoms on Pt_s sites is similar to that for H atoms. The increase in hydrogen uptake at 300 K following O_2 adsorption at 363 K may be due to an enhancement of hydrogen spillover. The amount of titratable oxygen created by N_2O decomposition at 363 K is less than that produced by exposure to O_2, but it still yields a Pt dispersion that is close to that based on H_2 chemisorption, although it is around 10% lower. Consequently, the H_2–N_2O titration method is applicable to more complicated catalyst systems. The necessity of conducting this latter reaction near 363 K is demonstrated by the experiment in which the Pt/C catalyst was exposed to N_2O at 300 K for the same time (30 min). Titration of this surface showed that the coverage of oxygen was substantially lower than that achieved at 363 K.

Few, if any, spectra have been reported for CO adsorbed on carbon-supported metals, and we are not aware of such data for Pt in the literature; however, the sensitivity of our modified DRIFTS cell allows us to record such information (74). After a given pretreatment, the CO spectra are distinctly different from those for Pt/SiO_2, especially those for CO on a clean, evacuated surface. The bands in Fig. 5a for linearly adsorbed CO are at much lower wavenumbers and smoothly overlap the region associated with bridge-bonded species. The explanation for this is not known at this time, but it could result from an interaction between the Pt crystallites and the carbon support. CO adsorption on the initially H-covered Pt surface produces a stronger IR band whose maximum has shifted to 2033 cm^{-1}, a value more commensurate with CO on Pt, and after several H_2–O_2 titration cycles at 300 K, CO adsorption increased further and the peak for linearly adsorbed CO is at a more typical value of 2046 cm^{-1}. Adsorption of CO on an O-covered surface obtained by a single exposure to O_2 at

300 K gives a similar, but less intense, spectrum. No evidence of CO adsorbed on oxidized Pt is seen.

SUMMARY

Despite conclusions reached from UHV studies of N_2O adsorption on Pt, this molecule decomposes on Pt surfaces at 363 K and pressures around 76 Torr to form a monolayer of chemisorbed oxygen. The monolayer coverage on a 0.81% Pt/SiO_2 catalyst was the same as that established by H_2 chemisorption and about 8% higher than that achieved by O_2 chemisorption at either 300 or 363 K. This oxygen was completely removed by H_2 titration at 300 K; thus reaction [4] describes this dissociative adsorption process well, and the combination of N_2O dissociation with H_2 titration offers an alternative approach to measure Pt dispersion. This new method is especially useful when O_2 can interact extensively with the support surface, and an example of this situation was demonstrated using a commercial 3% Pt/C catalyst. With this Pt/C catalyst, irreversible CO uptakes gave dispersions that were significantly lower than those obtained from the H adsorption and H titration methods; thus, the latter methods appear to measure Pt dispersion more accurately when supports having chemically complex and heterogeneous surfaces are used.

After O coverages were established by either N_2O decomposition at 363 K or O_2 adsorption at either 300 or 363 K, exposure of these SiO_2-supported Pt surfaces to CO at 300 K removed the oxygen via CO_2 formation, except for a small residual fraction of the surface which yielded a 2188 cm^{-1} peak indicative of CO on oxidized Pt_s sites, compared to the predominant peak at 2073 cm^{-1} for CO on reduced Pt. Characterization of the Pt/C catalyst was complicated by a major interaction between O_2 and the carbon surface that resulted in large irreversible oxygen uptakes; however, this problem was avoided by the use of N_2O decomposition to provide chemisorbed O on the Pt surface. A broad DRIFTS band for CO chemisorbed on this reduced Pt/C catalyst existed between 1950 and 2060 cm^{-1}; however, successive H_2–O_2 titration cycles at 300 K resulted in a narrower, more intense peak with a maximum near 2046 cm^{-1}. No evidence for oxidized Pt was observed in this catalyst after CO was adsorbed on an O-covered surface. Consequently, this CO titration reaction is adequately described by reaction [5], and when combined with other adsorption techniques, it may offer an approach to distinguish between surface atoms in certain bimetallic systems, such as Cu–Pt catalysts.

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