

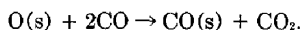
Surface Reaction for Measurement of Pt Dispersion on Supported Catalysts*

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The surface area of dispersed platinum on different supports has been measured by means of a "titration" technique involving the interaction between chemisorbed oxygen and carbon monoxide. This reaction proceeds rapidly at room temperature in accordance with the stoichiometry



Thus quantitative determination of the CO consumed and/or the CO₂ formed offers a suitable measurement of the number of oxygen atoms chemisorbed on the platinum surface. It is found that on bulk as well as supported Pt catalysts the maximum value of O/Pt = ½, so that quantitative information on the surface area on Pt may be obtained from the CO titration. Repeated exposures of a Pt/Al₂O₃ catalyst to molecular oxygen at room temperature followed by CO titration result in an apparent increase in Pt dispersion caused most likely by crystal reorientation.

INTRODUCTION

Of the various experimental procedures available for measuring the surface area of dispersed metal catalyst, the methods of physical adsorption (BET) and selective chemisorption have been used most widely, as reviewed in two recent publications (1, 2). An alternative procedure is the "titration" method in which the surface density of oxygen chemisorbed on platinum is determined by reaction with molecular hydrogen (3). Our recent studies (4) of the interaction between oxygen adatoms on a Pt surface and gaseous carbon monoxide suggest an extension of the surface area titration technique with CO as the reactant. Although similar in principle to the hydrogen titration (3), the experimental procedure based on CO permits quantitative

determination of the mass of titrant (CO) consumed as well as the mass of product (CO₂) formed, thereby offering an additional measure of the stoichiometry of the surface reaction. We have applied this CO/O(s) titration procedure to surface area measurements of bulk Pt and of Pt dispersed on alumina and carbon supports.

Studies of the surface interaction of oxygen and carbon monoxide with Pt demonstrated that in the case of Pt (4) and of Pd (5-7) rapid reaction occurs at room temperature between a surface adlayer of chemisorbed oxygen and gaseous carbon monoxide in accordance with the stoichiometry



where (s) refers to a surface-adsorbed species and (g) to a gaseous species. For every oxygen adatom, two molecules of CO are consumed. Thus CO-titration may be used to examine the surface area of the dispersed metal, once the maximum degree of metal

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coverage of the metal with oxygen has been established. Detailed oxygen sorption studies under ultra-high vacuum conditions (4) indicated that for a polycrystalline Pt surface at 300 K the limiting value of surface coverage corresponds to a ratio of $O/Pt = 1/2$, in agreement with the upper limit of adsorbed oxygen as reported by several investigators (8-10) working with well-defined Pt surfaces (in terms of surface cleanliness). Similarly for Pd, the LEED measurements (5) indicate a ratio of $O/Pd < 1$ and are interpretable in terms of a maximum oxygen coverage corresponding to $O/Pd = 1/2$ at 300 K.

EXPERIMENTAL DETAILS

The surface adsorbate titration experiments were carried out in a conventional BET apparatus (11) provided with a gas handling system for volumetric gas adsorption studies. The volume of gas adsorbed or reacted was determined from the change in gas pressure in a calibrated volume with a thermistor as a pressure sensor (12) calibrated for the various gases. The catalyst sample was contained in a small-volume side arm attached to the vacuum and gas-handling system. The sample could be pretreated under vacuum ($P \leq 10^{-6}$ Torr) by exposure to elevated temperatures to drive off surface adsorbates and to study sintering effects.

The contribution of the support material to the surface reaction was minimized by carrying out the surface reaction at room temperature. Thus after exposure to a known volume of molecular oxygen (exposure of 600 Torr sec or more), the sample chamber was pumped down to the background pressure ($P \leq 10^{-6}$ Torr). Then several aliquots of CO were admitted from a calibrated volume, which was provided with a U-tube cooled in liquid nitrogen for simultaneous collection of the CO_2 produced by the metal-catalyzed surface reaction. By this means, the likelihood of CO_2 adsorption on the support was reduced. Still, as will be shown in the following section, the Al_2O_3 support tended to adsorb some of the carbon dioxide. By heating of the catalyst to 480 K this CO_2 -

adsorbed on the support could later be desorbed and distilled into the U-tube. Separate experiments demonstrated that under these experimental conditions the support material acted merely as an adsorbent but did not contribute to the formation of CO_2 .

After no further uptake of CO, the cooled U-tube containing the trapped CO_2 was connected to the vacuum system for removal of residual gases. The U-tube was then isolated and allowed to warm up to room temperature. The resulting pressure of CO_2 was measured in the calibrated volume of the gas-handling apparatus.

For Pt, the catalyst samples were composed of (1) finely divided Pt particles prepared by the hydrazine reduction process, (2) a carbon-supported Pt catalyst (0.8 wt% Pt), and (3) an alumina-supported Pt catalyst* (0.6 wt% Pt/ Al_2O_3). For each of these samples the surface area was examined by means of the CO-titration technique and compared with the results obtained by other procedures. The unsupported Pt catalyst was pretreated at 573 K by exposing it to oxygen (1 atm, 1 hr), followed by evacuation ($< 10^{-6}$ Torr, 1 hr), exposure to hydrogen (1 atm, 1 hr), and finally evacuation ($< 10^{-6}$ Torr, 3 hr) before allowing it to cool to room temperature ($P \leq 10^{-6}$ Torr). The supported Pt catalysts were heated under vacuum ($< 10^{-6}$ Torr) at 625 K (1 hr) and then brought to room temperature for subsequent exposure to O_2 and CO.

EXPERIMENTAL RESULTS

In evaluating the feasibility of the experimental technique for surface-area measurement, we selected several dispersed Pt catalysts on different support materials. It proved useful to examine quantitatively the stoichiometry of the surface titration in terms of CO consumed and CO_2 produced. In addition we compared the surface area results obtained by the CO titration with those derived by BET (in the case of the unsupported Pt sample and by

* This catalyst was kindly supplied by Chevron Research Corporation.

TABLE 1
SURFACE AREA MEASUREMENTS OF Pt BY CO TITRATION OF CHEMISORBED OXYGEN^a

Catalyst	Temp (K)			Specific surface area (m ² /g _{Pt})		
	Reaction	CO ₂ Desorption	O/CO ₂	CO/CO ₂	CO Titration	Other
Pt powder	300	300	1.00	1.91	0.82	0.83
Pt/carbon (0.8 wt%)	300	300	6.23	2.05	6.45	—
Pt/Al ₂ O ₃ (0.6 wt%) ^b	300	300	7.25	11.4	147	152 ^b
	300	480	1.30	2.03	147	152 ^b

^a O(s) + 2CO(g) → CO₂(g) + CO(s).

^b Catalyst supplied by Chevron Research Corp.

CO adsorption (for the alumina-supported metal catalyst).

The results, shown in Table 1, demonstrate that for finely divided Pt the surface reaction between chemisorbed oxygen and gaseous CO proceeds at 300 K in accordance with the stoichiometry given by Eq. (1). In addition the BET (krypton) adsorption measurements yield a surface area in excellent agreement with that derived from the CO titration.

Similar considerations apply to the Pt catalyst on a carbon support. Again the CO/CO₂ ratio is found to be near a value of two, although a fraction of the oxygen sorbed ends up on the support, where it remains inactive toward the CO added in the subsequent step.

For the Al₂O₃-supported Pt catalyst, the CO/O reaction proceeds readily at 300 K. However, only a portion of the CO₂ produced is recovered under these conditions, while the remaining fraction stays adsorbed on the support. By raising the temperature of the sample to 480 K, the remaining CO₂ can be recovered and the proper mass-balance ratio of CO/CO₂ = 2 obtained. In comparing the results of the surface area determination by CO titration with those obtained from CO-adsorption studies, we take into account the fact that saturation coverage with CO corresponds to a maximum occupation of 80% of the sites on a polycrystalline Pt surface (4). The surface area of 152 m²/g of Pt so calculated for CO adsorption agrees with the value derived from CO titration (147 m²/g_{Pt}). We may conclude that for each

of the Pt systems studied the mass of CO reacted with chemisorbed oxygen offers a reliable measure of the number of surface sites when account is taken of the stoichiometry of the surface reaction [Eq. (1)].

DISCUSSION

For determining the Pt surface area, the experimental procedure of titrating chemisorbed oxygen with CO must satisfy three requirements. First, the maximum degree of surface coverage (saturation coverage) with chemisorbed oxygen must be known, i.e., the ratio O/Pt must be established in order to relate the CO consumed (and/or the CO₂ formed) to the surface site density of the metal. Second, the stoichiometry and the rate of the surface reaction must be known. Third, it must be ascertained whether the chemisorption of oxygen (13, 14) or the surface reaction with CO affects the metal dispersion.

As for the O/Pt ratio, the data reported in the literature cover a range $\frac{1}{2} \leq \text{O/Pt} \leq 1$. This variation appears to be interpretable in terms of differences in crystallographic orientation. As shown by Tucker (8) on Pt(111), the ratio O/Pt = 1:2 prevails. Similarly, on polycrystalline Pt samples (4, 9, 10, 15, 17) (films and ribbons) the same ratio applies possibly because of the predominance of low index planes under these conditions. For supported Pt catalysts, the crystallographic orientation of the dispersed metal is not known. However, the data of Mears and Hanford (18) and of Wilson and Hall (19) indicate that dispersed samples chemisorb only half as

much oxygen as hydrogen. If for such dispersed samples the $H/Pt \approx 1$, as is considered likely (19), one is led to conclude that for saturation coverage $O/Pt \approx 1:2$ is a reasonable approximation especially for heat-treated samples, which would tend toward the thermodynamically favored Pt(111) crystal orientation.

The surface reaction between oxygen chemisorbed on Pt and gaseous CO and the stoichiometry associated with it are fairly well established (4). While oxygen adatoms can undergo this reaction rapidly at room temperature, chemisorbed carbon monoxide does not react with gaseous oxygen (4, 5, 20). Also our kinetic data show no evidence for CO oxidation involving sorbed O_2 molecules as suggested in reference 20. It is of interest that in the absence of preadsorbed oxygen the CO flash-desorption experiments (4) indicate a saturation coverage of 80% of the available surface sites (9×10^{14} CO molecules/cm² Pt) and two predominant binding states, which are interpreted in terms of a distribution between linear- and bridge-bonded CO. However, during the CO titration of oxygen atoms chemisorbed on Pt, the reaction follows quantitatively a stoichiometry in which each oxygen adatom is replaced by one sorbed CO molecule (in addition to the CO molecule lost by surface reaction). Thus the maximum CO surface coverage following the CO titration is $CO/Pt = 0.5$ rather than 0.80 as observed in the CO adsorption studies on clean Pt surfaces (4).

The adsorption of oxygen appears to cause surface reconstruction, which modifies the number of binding sites available for subsequent CO adsorption. This effect is reminiscent of the reported enhancement of hydrogen chemisorption on Pt supported on carbon (21) or alumina (14, 22) after pretreatment in oxygen. Such change in the number density of bonded hydrogen atoms or CO molecules may be due to crystal rearrangement brought about by oxygen exposure of the Pt to oxygen. Possibly such surface reconstruction results in the formation of atomic steps and terraces (23) that favor dissociation and chemisorption of

TABLE 2
EFFECT OF SUCCESSIVE OXYGEN EXPOSURES
ON SURFACE AREA OF Pt CATALYST^a

Number of exposures to oxygen ^b	Reactant surface titration (molecules $\times 10^{18}/g_{cat}$)		Specific surface area ^c (m ² /g _{Pt})
	O ₂	CO	
1	2.99	9.48	141
2	2.99	9.85	146
3	3.14	10.06	150
4	3.10	10.11	151
5	3.06	10.40	155

^a Pt (0.6 wt%)/Al₂O₃; catalyst supplied by Chevron Research Corporation.

^b Oxygen pressure = 0.25 Torr.

^c Based on an average surface site density of 1.12×10^{16} Pt atoms/cm².

hydrogen (24). At the same time such rearrangements of lattice atoms on an atomic scale may cause displacement and formation of surface structures favorable for CO adsorption, especially of bridge-bonded species.

To examine the effect of oxygen pretreatment on metal dispersion, we subjected a sample of alumina-supported Pt catalyst to a series of successive oxygen exposures (250 μ m O₂) and CO-titrations at 300 K

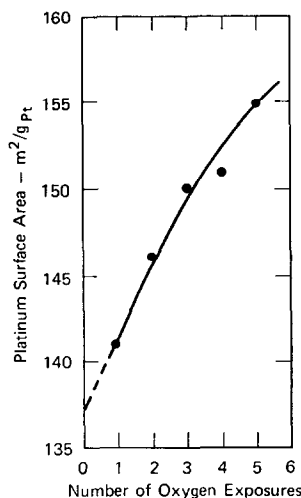


FIG. 1. Surface area of alumina-supported catalyst (0.6 wt% Pt on Al₂O₃) after several exposures to oxygen (0.25 Torr).

and evaluated the corresponding Pt-surface areas. Between each titration the catalyst was heated at 620 K to desorb the residual chemisorbed CO before admission of oxygen at room temperature. The results of five successive O(s)/CO titrations are shown in Table 2. The mass of CO reacted exhibits a monotonic rise, suggestive of an increase in metal surface area of nearly 10% after five oxygen exposures. By extrapolation one obtains a "virtual" surface area of 137 m²/g_{Pt} for the catalyst at "zero exposure" to oxygen (Fig. 1).

Finally it should be pointed out that the CO/O(s)-titration technique is not limited to Pt but may be extended to other dispersed metals. Work is in progress to explore its applicability to other metal and mixed-metal catalysts.

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