

화학흡착에 의한 백금 및 백금-텅스텐 진공 증착막의 표면적 측정*

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Surface Area Measurement by Chemisorption of Gases on Vacuum Evaporated thin Film of Platinum-Tungsten Film**

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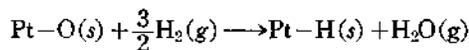
요 약. 백금 백금-텅스텐 증착막에 의한 수소, 일산화탄소의 화학흡착과 화학흡착시킨 산소의 수소 titration 을 110 °C 에서 실험해본 결과, H₂/O₂ titration 방법에 의한 백금-텅스텐 증착막에서의 백금 표면적 측정이 가능한 것 같다.

ABSTRACT. The chemisorption of hydrogen and carbon monoxide, as well as the hydrogen titration of prechemisorbed oxygen was studied at 110 °C on evaporated platinum and platinum-tungsten films. The results suggest that hydrogen titration of prechemisorbed oxygen may be used to determine the platinum surface area of platinum-tungsten film.

INTRODUCTION

Selective chemisorption of gases, mainly hydrogen and carbon monoxide, has been used to determine the surface area of metal dispersed on different supports. Selective chemisorption seems to be the only technique applicable to measure the metal dispersion in case the metal crystallite size is too small to be measured by X-ray technique. Chon, *et al.*¹ studied the calorimetrically indicated titration of oxygen and hydrogen on platinum black at 0°C and interpreted the results on the hydrogen titration of oxygen-prechemisorbed

platinum in terms of the following reaction.



Benson & Boudart² applied the hydrogen-oxygen titration method to the measurement of supported platinum surface area. H₂/O₂ titration on Pt and on supported Rh is reported elsewhere³⁻⁵. The advantage of the titration technique lies in the increase of sensitivity and in the simplicity of the measurement. In this study the possibility of determining the platinum surface area of the platinum-tungsten film by using the titration of chemisorbed oxygen with hydrogen is investigated.

*This work was done at Mobil Research & Development corporation, Princeton, N. J., U. S. A.

EXPERIMENTAL

Thin films of platinum and platinum-tungsten are being vacuum deposited on the surface of glass vessels. The source of vapor is a U shaped platinum wire (B & S 26 gauge) or a platinum-tungsten wire (0.016") spot welded to tungsten lead wires. Fig. 1 shows the arrangement for film deposition. The films are pretreated at 450 °C in high vacuum before adsorption measurements. Hydrogen (99.999%), carbon monoxide (99.9%) and krypton (99.995%), research grade from Matheson Gas Products, and oxygen (99.996%), research grade from Lif-O-Gen. Inc. were passed through a liquid nitrogen trap before use. Chemisorption of hydrogen and carbon monoxide and H₂/O₂ titration was studied at 110 °C. The adsorption vessel which is provided with a cold finger immersed in liquid nitrogen to trap water or carbon dioxide formed. Pressure is measured with a capacitance manometer or a thermistor vacuum gauge. The thermistor vacuum gauge was constructed using a matched pair of thermistors and was calibrated against a McLeod gauge for individual gases.

RESULTS and DISCUSSION

Fig. 2 shows the uptake of hydrogen and carbon monoxide by platinum film and of hydrogen by oxygen-prechemisorbed platinum surface. The uptake of hydrogen (2.02×10^{-3} cc)

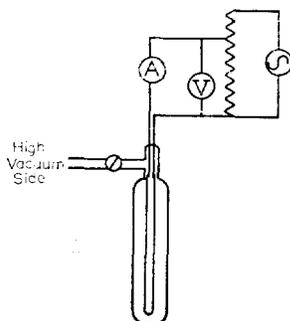


Fig. 1. Film deposition arrangement.

by the oxygen-prechemisorbed surface is due to the reaction of chemisorbed oxygen with hydrogen and subsequent chemisorption of hydrogen on the oxygen-free platinum surface (0.20×10^{-1} cc). The difference in the amount of hydrogen uptake between the oxygen-prechemisorbed surface and the oxygen free surface (1.82×10^{-3} cc) corresponds to 42cm² of platinum surface area using 8.4Å²* as an average area for a surface platinum atom, assuming the surface reaction of PtO(s) + H₂ → Pt + H₂O. Studies on CO chemisorption on platinum/silica shows that the ratio (Pt atom exposed) / (CO molecules adsorbed) varies from ~1 to ~2 with increasing platinum content⁶. It is suggested that the Pt/CO ratio depends on the crystallite size, and that CO may be present in bridged form on large crystallites and linear form on highly dispersed platinum. On evaporated platinum films it is assumed that

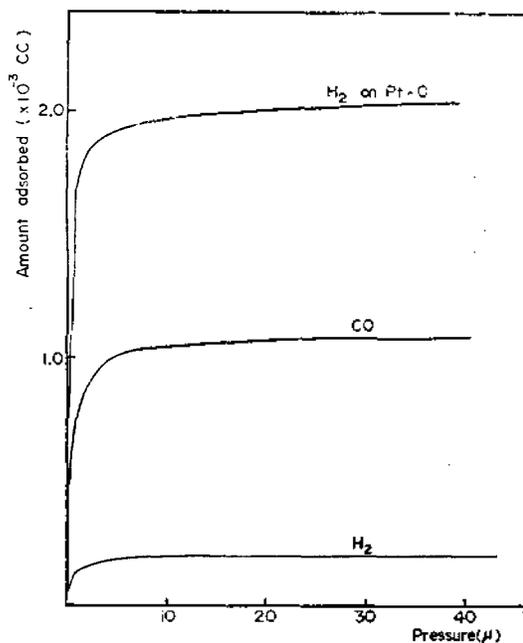


Fig. 2. Uptake of hydrogen and carbon monoxide by platinum film and of hydrogen by oxygen-prechemisorbed platinum surface at 110 °C.

*This area was obtained by averaging the area of the platinum atoms present in the (100) (110) and (111) crystallographic planes.

Table 1. Surface area of the platinum and platinum-tungsten Films.

	Platinum	Platinum-Tungsten
Hydrogen titration	42 cm ²	25 cm ²
CO Chemisorption	49 cm ²	28 cm ²
BET(Krypton)	52 cm ²	65 cm ²

CO is assumed that CO is chemisorbed primarily in bridged form. Assuming, the bridged form, uptake of $1.05 \times 10^{-3} \text{ cm}^3$ of CO by platinum film corresponds to 49 cm² of platinum surface area. The slight discrepancy in the value of platinum surface area obtained from H₂/O₂ titration and CO chemisorption may be attributed to the presence of two different forms of CO on the surface.

The uptake of hydrogen by oxygen prechemisorbed platinum-tungsten films at 110°C is much less ($1.2 \times 10^{-3} \text{ cm}^3$) than the uptake by platinum films (2.02×10^{-3}), even-though the krypton BET area of platinum-tungsten film is larger (65 cm²) than that of platinum (52 cm²) as shown in the Table 1. The Hydrogen titration of prechemisorbed oxygen takes place readily even at room temperature. If we assume that the oxygen chemisorbed on tungsten is not removed by hydrogen at 110°C, the hydrogen uptake of $1.2 \times 10^{-3} \text{ cm}^3$ by oxygen prechemisorbed platinum-tungsten may be regarded as the result of hydrogen titration of oxygen-prechemisorbed platinum

sites. The uptake of $1.2 \times 10^{-3} \text{ cm}^3$ then corresponds to 24cm² of platinum area.

On a platinum-tungsten film at 110°C the rapid adsorption of CO is followed by a slow uptake. The slow uptake of CO was not observed for platinum film at 110°C. The nature of the slow uptake is not clear. If we take the amount of rapid uptake of CO as the amount taken up by platinum, uptake of $0.58 \times 10^{-3} \text{ cc}$ corresponds to 25 cm² of platinum area. This compares well with the value obtained from H₂/O₂ titration on platinum-tungsten film.

The results suggest that the selective hydrogen titration of chemisorbed oxygen may be used to determine the platinum surface area of platinum-tungsten films.

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