

## Short Communication

# Effect of surface modification on adsorption properties of metal surfaces

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### Abstract

Using a two-dimensional model of electron gas-adsorbate particle interaction, energy of physical adsorption and chemisorption dependence on modifying adsorbate coverage is described. Experimental study of physical adsorption of argon on Pd and Ag surfaces at  $-196^{\circ}\text{C}$  shows that preadsorption of oxygen increases adsorption capacity of uncovered part of the metal surface, which is in agreement with the theory. A study of thermal desorption of CO and H<sub>2</sub>O from Ag surface and nitrogen and H<sub>2</sub>O from Pd surface shows an increase in activation energy desorption of these gases from modified surfaces.

**Key words:** Physical adsorption, chemisorption, activation energy of desorption.

## 1. Introduction

Analysing a two-dimensional model of electron gas-adsorbate particle interaction on metal surface, Yagodovskii and Ray<sup>1</sup> found that small coverage preadsorption of certain gases increases electron density of the uncovered surface. They derived an equation for calculating two-dimensional electron density  $n_e$  of the metal surface

$$n_e^2 + n_e \left( 2 \frac{B_{12}}{B_{11}} n_o \theta + 1 \right) - n_e^{02} = 0 \quad (1)$$

where  $B_{11}$  is the second virial coefficient of conduction electron interaction together,  $B_{12}$  is the second virial coefficient of electron gas-adsorbate particle interaction,  $n_e^0$  is the electron density of the bare metal surface,  $n_o$  is the surface atomic density of the bare metal surface and  $\theta$  is the surface adsorbate coverage.

Change of electron density should influence adsorption potential in the case of physical adsorption as energy of adsorption depends on this parameter<sup>7,3</sup>. Mavroyannis<sup>2</sup> found that energy of interaction between a neutral atom and a metal surface is proportional to the electron density of the metal surface.

$$Q = \frac{\sqrt{\alpha} N}{8 R^3} \cdot \frac{h w / \sqrt{2}}{N / \alpha + h w / \sqrt{2}} \quad (2)$$

where  $w = \sqrt{4 \pi e^2 / m \cdot n_e^{3/4}}$  is the characteristic resonance frequency of adsorption of the electrons in the metal,  $\alpha$  is the static adsorbate polarizability,  $N$  is the number of electrons in the adsorbate atom, and  $R$  is the distance between the centre of the adsorbed atom and the metal surface.

Lang and Kohn<sup>4</sup> using density functional formalism in the Jellium model approximation have described chemisorption on metal surfaces. Using linear response theory, they have derived an equation for chemisorption energy of a point charge  $q$  at a distance  $X_1$  from the metal surface

$$E = - \frac{q^2}{4 (X_1 - X_0)} \quad (3)$$

where effective location of the metal surface in the Jellium model ( $X_0$ ) is connected with the conduction electron density ( $n_e$ ) of the metal surface through the Wigner Seitz radius<sup>5</sup> ( $r_s$ )  $x_0 \sim 1/r_s \sim n_e$ . We have experimentally verified the theoretical predictions about change of adsorption potential during physical adsorption and chemisorption on modified metal surfaces and the results are presented here.

## 2. Results and discussion

**2.1 Physical adsorption:** Low temperature adsorption of argon on thin Pd and Ag films was studied. Oxygen was used as modifying adsorbate. Adsorption isotherms were measured by the capillary flow method<sup>6</sup>. Surface coverage by oxygen was calculated by assuming that one oxygen atom adsorbs on one metal atom, and also the roughness coefficient 6.9 for Pd<sup>7</sup> and 5.0 for Ag surfaces<sup>8</sup>. Metal surfaces were modified by treating with oxygen at  $-90^\circ \text{C}$  for Pd and  $-196^\circ \text{C}$  for Ag. In such conditions, according to Czanderna<sup>9</sup> and Dus<sup>10</sup>, oxygen is not dissolved in bulk, but remains adsorbed on the surface only. Adsorption isotherms of argon on Pd and Ag films, before and after modification of the surface by oxygen, are presented in fig. 1. It can be seen from the figure that preadsorption of a small quantity of oxygen ( $\theta = 0.1$ ) increases adsorption capacity in both the cases. Adsorption isotherms were treated with the help of a polynomial

$$\Gamma = B_1 P + B_2 P^2 \quad (4)$$

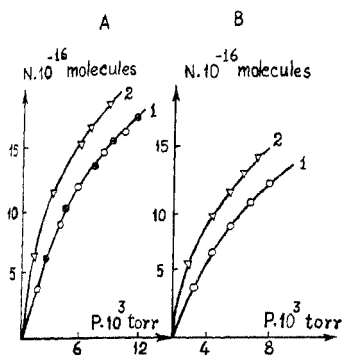


FIG. 1. Adsorption isotherms of argon at  $-196^{\circ}\text{C}$ .

A—on Pd films

B—on Ag films

1—Bare metal surface

2—Modified metal surface ( $\theta_{\text{oxygen}} = 0.1$ )

(These points are shown by crossed circles in fig. 1). Here  $\Gamma$  is the surface concentration of the adsorbate and  $B_2$  is the second virial coefficient of the adsorbate particle interaction together. Henry coefficients before ( $B_0$ ) and after modification ( $B_1$ ), were calculated by the least square method and the increase was found to be 21% for Pd and 30% for Ag. Our calculation shows an increase in heat of adsorption as a result of surface modification,

$$Q = Q - Q_0 = RT \ln B_1 / B_0 \quad (5)$$

of 38.5 cal/mol for Ag and 28.6 cal/mol for Pd films. Here  $Q_0, Q$  are the heats of adsorption before and after surface modification.

**2.2 Chemisorption:** In the chemisorption experiments with thin Pd and Ag films at first ethylene was used as a modifying adsorbate. Metal surfaces were treated with ethylene vapour at  $500^{\circ}\text{C}$  (Pd) and  $400^{\circ}\text{C}$  (Ag). Metal surface coverages with ethylene were calculated to be of the order  $\sim 0.1 - 0.18$ . The following experiments were then carried out on the modified surfaces.

1. Thermal desorption of nitrogen was studied in the interval of  $380 - 500^{\circ}\text{C}$  on the modified Pd surface.
2. Thermal desorption of CO was studied in the interval of  $360 - 500^{\circ}\text{C}$  on modified Ag surface.

In another set of experiments, CO was used as modifying adsorbate. Water desorption was studied on modified surfaces in the interval of 95-255°C for Pd and 180-300°C for Ag surfaces.

In all these experiments, temperature was raised at the rate of  $20 \pm 1.5^\circ\text{C}$  per minute. Desorption velocity ( $W_D$ ) was measured for a few different values of constant temperature, and activation energy of desorption ( $E_D$ ) was calculated using the formula

$$W_D = K_0 \cdot \theta \cdot e^{-E_D / RT} \quad (6)$$

where  $K_0$  is the frequency factor.

Figures 2 and 3 show dependence of the rates of velocity of desorption of different systems in linear coordinates of eqn. 6, where  $K = W_D / \theta$ . Results indicate that primary modification of metal surface with small amount of adsorbate increases the activation energy of desorption. Activation energy of desorption was calculated by the least square method. The significance of different values of  $E_D$  was estimated. From the results shown in Table I it is seen that  $E_D$ , a characteristic of chemisorption energy which is in agreement with theoretical eqn. 3, increases after primary modification of the metal surface by a small amount of adsorbate.

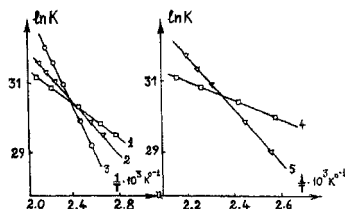


FIG. 2.  $\ln K$  vs  $1/T$ .

A-Pd surface

1-Nitrogen on bare metal surface

2-Nitrogen on modified metal surface  
( $\theta \text{ C}_2\text{H}_4 = 0.1$ )

3-Nitrogen on modified metal surface  
( $\theta \text{ C}_2\text{H}_4 = 0.18$ )

B-Ag surface

4-CO on bare metal surface

5-CO on modified metal surface  
( $\theta \text{ C}_2\text{H}_4 = 0.15$ )

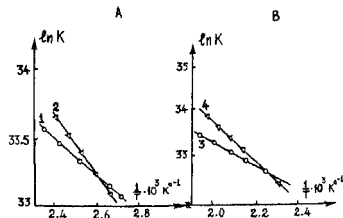


FIG. 3.  $\ln K$  vs  $1/T$ .

A-Pd surface

1-H<sub>2</sub>O on bare metal surface

2-H<sub>2</sub>O on modified metal surface ( $\theta \text{ CO} = 0.1$ )

B-Ag surface

1-H<sub>2</sub>O on bare metal surface

2-H<sub>2</sub>O on modified metal surface ( $\theta \text{ CO} = 0.11$ )

Table I

## Chemisorption changes of different systems due to surface modification

Modifying adsorbate	Adsorbate adsorbent system	Modifying adsorbate coverage $\theta$	$E_D$ kcal/mol	
C <sub>2</sub> H <sub>4</sub>	CO-Ag	0	19.5	± 1.4
C <sub>2</sub> H <sub>4</sub>	CO-Ag	0.15	25.7	± 1.9
C <sub>2</sub> H <sub>4</sub>	N-Pd	0	10.5	± 0.8
C <sub>2</sub> H <sub>4</sub>	N-Pd	0.1	13.9	± 1.7
C <sub>2</sub> H <sub>4</sub>	N-Pd	0.18	21.7	± 0.6
CO	H <sub>2</sub> O-Ag	0	7.84	± 1.63
CO	H <sub>2</sub> O-Ag	0.11	11.24	± 2.19
CO	H <sub>2</sub> O-Pd	0.1	3.63	± 0.27

## 3. Conclusion

It has been shown that as a result of change of electron density of uncovered surfaces, adsorption potential of physical adsorption and energy of chemisorption increase. This is in good agreement with theoretical predictions.

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