Chemisorption of Nitrogen Oxide and Nitrogen on Tungsten

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The chemisorption of nitrogen oxide and nitrogen on a polycrystalline tungsten filament was studied using flash desorption mass spectroscopy. The saturation coverage for nitrogen oxide and nitrogen on tungsten is 8.8×10^{14} molecules/cm^2 and 1.9×10^{14} molecules/cm^2, respectively. These saturation coverages on tungsten are about 1.7 times those on rhenium. The initial sticking probability of nitrogen oxide is very high compared with other gases. It is assumed that the nitrogen oxide adsorption is non-dissociative on tungsten, while the nitrogen is adsorbed dissociatively. When the temperature of the tungsten filament saturated with nitrogen oxide is raised, a small amount of nitrogen oxide molecules desorb at about 475 K, and dissociation occurs at more elevated temperatures. The greater part of the nitrogen desorbs before the temperature reaches 1500 K. No oxygen desorption was detected upon heating the tungsten saturated with nitrogen oxide. It appears that oxygen probably desorbs as tungsten oxide. Three states of nitrogen desorption, designated α, β_1, and β_2, on tungsten appeared at room temperature. The activation energy of the desorption for the strongly chemisorbed nitrogen of the β_1 and β_2 states on tungsten are 78 kcal/mol and 80.5 kcal/mol, respectively.

Fundamental to the understanding of heterogeneous reactions, such as catalytic reactions, is the determination of the role of the surface and the dependence of the reaction variables on the properties of the solid. Recently, detailed data of chemisorption studies have been presented taking advantage of the progress of ultra-high vacuum techniques and the development of modern methods,[1-5] such as the use of flash filaments, isotopic mixing, FEM, FIM, LEED and AES.

Many studies of chemisorption of common gases on tungsten have been made, but there have been only a few studies of the chemisorption of nitrogen oxide.[6-9]

In the present investigation, the chemisorption of nitrogen oxide and nitrogen on a tungsten filament was studied using flash desorption mass spectroscopy.

Experimental

The ultra-high vacuum apparatus used in this study is similar to that used in previous work[10,11] except that the reaction vessel with a volume of 1.0 l contained a polycrystalline tungsten filament with a geometrical surface area of 1.26 cm^2. The tungsten filament was analyzed spectroscopically. (Found: Mo, 0.08%; Mg, 0.004%)

The total pressure was measured by means of a Pirani gauge with a sensitivity of 7.2×10^{-8} Torr/μV for N_2 and NO, and 7.5×10^{-8} Torr/μV for O_2. An omegatron mass spectrometer was used for analyzing the gaseous component and for measuring the partial pressure in the reaction vessel; it has a sensitivity of 12 Torr^{-1} and 11.8 Torr^{-1} for N_2 and NO, respectively. A B-A gauge was used only for the ultimate-pressure measurement, because the nitrogen oxide was dissociated by the hot filament of the gauge.

The temperature of the tungsten filament was measured by the same method as that reported in a previous paper.[10] The nitrogen oxide and nitrogen were also prepared by the method described in that paper, and no impurities up to mass 200 were detected by means of the omegatron mass spectrometer.

The ultimate pressure, read on a B-A gauge, was 3×10^{-10} Torr in the reaction system after rigorous outgassing. Before the experiment, the tungsten filament was heated to 2200 K in an oxygen atmosphere of about 1×10^{-6} Torr for a long time, in order to remove carbonaceous surface contamination.

The procedure used for the present experiments are also similar to that previously described.[10] The number of molecules of nitrogen oxide or nitrogen that strike the tungsten filament during the adsorption process is calculated from the recorder trace of the omegatron or the Pirani gauge. The amount of adsorbed molecules is calculated from the pressure and the volume of the reaction vessel when the filament is flashed at 2200 K in the closed system. In the case of the adsorption of nitrogen oxide, the number of molecules adsorbed is twice the number of molecules desorbed, because the desorbed gas is nitrogen.

After the adsorbed layers were formed, the temperature of the tungsten filament was raised slowly with an approximately linear sweep rate while the system was being evacuated. During that period, the ion currents of the omegatron mass spectrometer for each mass were recorded on a chart recorder.

Results and Discussion

Sticking Probability and the Amount of Adsorbed Nitrogen Oxide and Nitrogen on Tungsten. The relation between the number of molecules impinging on the filament, $N_{(e)}$(exposure), at various temperatures and those adsorbed, N, is shown in Fig. 1. The saturation coverage for nitrogen oxide is 8.8×10^{14} molecules/cm^2 at 300 K, which is much higher in comparison with that on rhenium. For adsorption on a tungsten filament at elevated temperatures, the saturation coverage of nitrogen oxide decreases as shown in Fig. 1. There are 8.2×10^{14} and

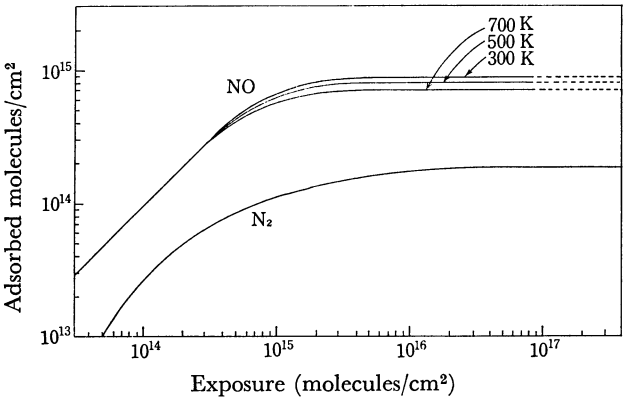

Fig. 1. Surface coverage as a function of exposure.

7.0×10^{14} molecules/cm^2 at 500 K and 700 K, respectively.

For the sake of comparison with nitrogen oxide adsorption, the adsorption of nitrogen was studied on the same tungsten filament. The saturation coverage of nitrogen on tungsten is 1.9×10^{14} molecules/cm^2, as is shown in Fig. 1. The saturation coverage for nitrogen oxide is 4.6 times as much as that for nitrogen. This ratio agrees with that on rhenium.[10] Assuming that the number of metal surface atoms is 1.5×10^{15} atoms/cm^2, this is equivalent to a W: NO ratio of about 2: 1. Yates *et al.*[6] state that the saturation coverage for nitrogen oxide on tungsten is 1.4×10^{15} molecules/cm^2, which is obtained from the ratio of the areas of the desorption spectrum of the nitrogen oxide monolayer to that of the nitrogen monolayer and from Ehrlich's data[12] for the adsorption of nitrogen on tungsten. Since saturation coverages of nitrogen on polycrystalline tungsten of 1.25 to 3.0×10^{14} molecules/cm^2 have been found by many investigators, as listed in Table 1, a comparison of the saturation coverage for nitrogen oxide and nitrogen should be made using the same tungsten filament.

Table 1. Comparison of initial sticking probabilities, saturation coverages and activation energies for nitrogen desorption

Investigator	s (initial)	Saturation coverage (molecules/cm^2)	E_d (kcal/mol)	Ref.
Schlier	0.42	1.8×10^{14}	—	13
Ehrlich	0.3	2.8×10^{14}	—	14
Hickmott	0.26	1.8×10^{14}	β: 81	15
Oguri	0.2	1.25×10^{14}	ε: 84 ζ: 69	16
Rigby	0.4	1.5×10^{14}	β_1: 73 β_2: 75	17
Yates, Jr.	—	1.6×10^{14}	β_1: 82 β_2: 84	18
Madey	—	—	β_1: 80 β_2: 82, 89	19
King	0.61	3.0×10^{14}	—	20
Tamura	0.35	1.9×10^{14}	β_1: 78 β_2: 80.5	This work

From the curve in Fig. 1, the sticking probability, s, can be calculated by means of the following equation:

$$s = \mathrm{d}N/\mathrm{d}N_{(e)}.$$

The relationship between the sticking probability and the surface coverage for nitrogen oxide is shown in Fig. 2. The initial sticking probability for nitrogen oxide adsorption on tungsten is close to unity up to $\theta\simeq0.4$ (θ is the monolayer fraction). This value agrees well with that found for the 110 surface of tungsten single crystals.[9] The initial sticking probability for nitrogen adsorption on tungsten obtained from Fig. 2 is 0.35, which is reasonable value in comparison with those of other papers.[13–17] Furthermore, the result obtained by the usual method, using flash desorption at a constant flow rate,[21] also agree with those of the present method. As in the case of the Re–NO system, one of reasons for such a high value of the initial sticking probability is that the ionization potential of nitrogen oxide (9.5 eV)[22] is lower than those of nitrogen ($\approx$16 eV), oxygen ($\approx$15 eV) and carbon monoxide ($\approx$14 eV).

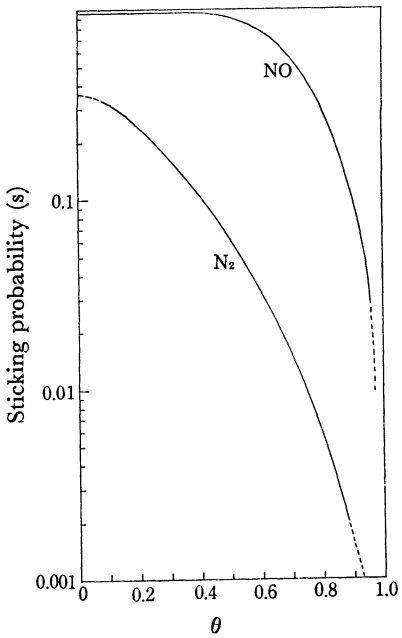

Fig. 2. Sticking probability as a function of surface coverage.

Rate of Adsorption and Desorption of Nitrogen Oxide and Nitrogen on Tungsten. It was confirmed that the rate of adsorption depends on the first power of the pressure. The rate of adsorption at constant pressure and temperature may, then, written as:

$$\mathrm{d}N/\mathrm{d}t = K\cdot P(1-\theta)^n,$$

where K and n are constants and P is the pressure of the nitrogen oxide or nitrogen. It was found that the rate of nitrogen oxide adsorption is proportional to $(1-\theta)$ as is shown in Fig. 3, and it seems that nitrogen oxide molecules are adsorbed non-dissociatively on tungsten. Nevertheless, for nitrogen adsorption, it may be shown that the adsorbed nitrogen was present in a dissociated form, because the rate of adsorption was proportional to $(1-\theta)^2$, as is shown in Fig. 3.

On the other hand, when the nitrogen oxide adsorbed is desorbed at definite temperature in a closed system,

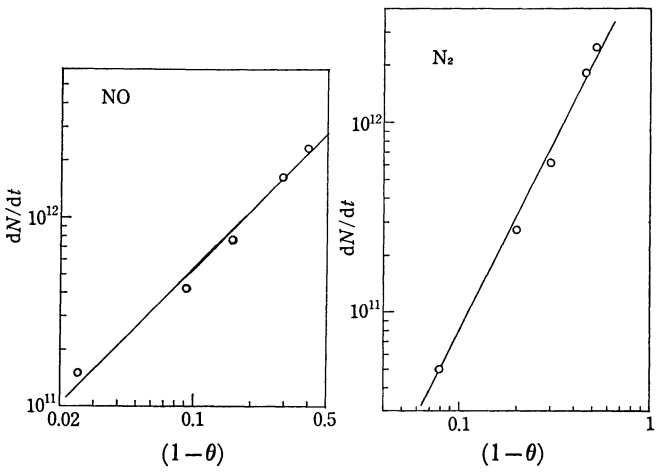

Fig. 3. The relation between the rate of adsorption and $(1-\theta)$.

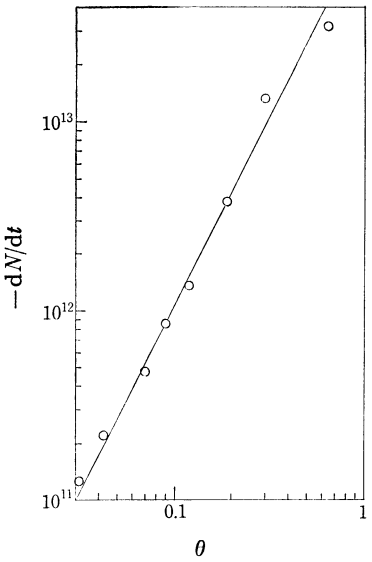

Fig. 4. The relation between the rate of nitrogen desorption and θ.

the rate of desorption may be expressed simply as:

$$-dN/dt = K'\theta^{n'},$$

where K' $[=\nu\exp(-E/RT)]$ is a constant and n' is the order of the desorption. In the W–NO system, the nitrogen oxide is decomposed for an increase in the tungsten temperature and is desorbed as in the case of nitrogen. The relation between the desorption rate and the surface coverage is shown in Fig. 4. As can be seen, the nitrogen desorption rate from a nitrogen oxide layer is roughly proportional to θ^2. At such high temperature, re-adsorption can be neglected.

Desorption Spectra. *1) Desorption from a Nitrogen Oxide Monolayer on Tungsten*: When tungsten saturated with nitrogen oxide was heated, nitrogen oxide and nitrogen from the tungsten surface due to decomposition of the nitrogen oxide desorbed, but neither molecular nor atomic oxygen were detected by means of the omegatron mass spectrometer. The desorption spectra from a nitrogen oxide monolayer on tungsten are shown in Fig. 5.

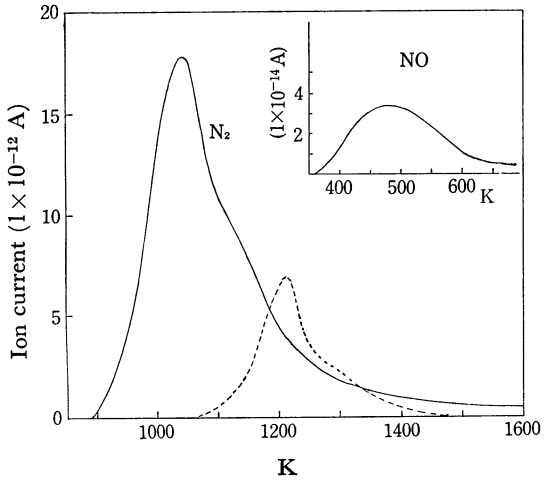

Fig. 5. The desorption spectra from nitrogen oxide monolayer. Dashed curve denotes nitrogen from nitrogen monolayer.

TABLE 2. THE T_p OF NO AND N_2, AND THE AMOUNT OF DESORBED GAS FROM A MONOLAYER
(The percentages being calculated in terms of adsorbed NO)

	T_p (K)	%
NO	475	0.3
N_2	1045	99.7

The temperature of the desorption-peak maximum, T_p, for nitrogen oxide and nitrogen in each desorption spectrum, and the percentage calculated in terms of the adsorbed nitrogen oxide are shown in Table 2. Desorption of nitrogen oxide began at about 350 K, and above 900 K no further desorption of nitrogen oxide was observed. Moreover, when the initial coverage of nitrogen oxide was changed, no desorption of nitrogen oxide was observed below 0.75 nitrogen oxide monolayer. The greater part of the nitrogen from the nitrogen oxide monolayer desorbed before the temperature reached 1500 K. The T_p of the nitrogen desorption from a nitrogen oxide monolayer was lower than that from a nitrogen monolayer by about 170 K. Although Yates *et al.*[6] have observed the desorption of oxygen from a nitrogen oxide monolayer on tungsten, no oxygen desorption was seen in the present experiment. It appears that the oxygen from the nitrogen oxide monolayer evaporates as tungsten oxide.

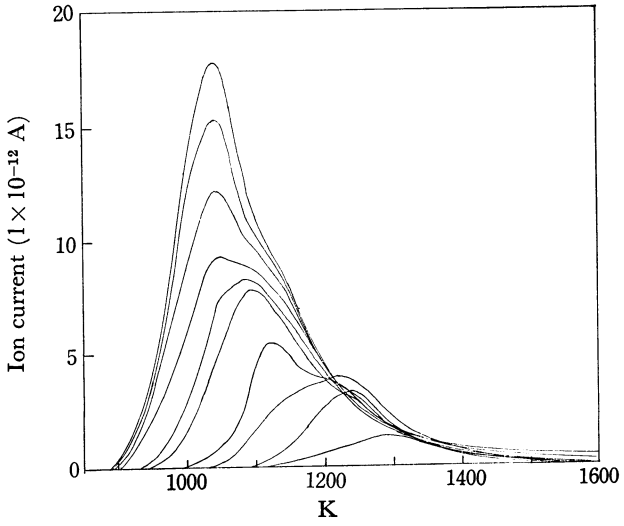

Fig. 6. The desorption spectra of nitrogen from various initial coverages of nitrogen oxide.

2) Desorption of Nitrogen from Various Initial Coverages of Nitrogen Oxide on Tungsten: The desorption spectra as a function of initial coverage of nitrogen oxide at 300 K are shown in Fig. 6. The desorption spectra for very low coverages of nitrogen oxide ($\theta<0.1$) resemble those for very low coverages of nitrogen. The T_p at $\theta=0.1$ and $\theta=0.2$—0.3 for nitrogen oxide adsorption correspond to the β_2 and β_1 peaks of the nitrogen desorption spectrum for a nitrogen layer on tungsten, respectively.

This behavior is reasonable, since the dissociation of nitrogen oxide for a very low coverage would produce a dilute layer of adsorbed nitrogen and oxygen (or oxide),

the desorption of nitrogen should be unaffected by the small amount of oxygen (or oxide) coverage. When the coverage of nitrogen oxide is increased, two new modes, ω_2(T_p: $\approx$1100 K) and ω_1 (T_p: 1045 K) peaks as designated by Yates *et al.*,[18] appeared which were formed beginning at about θ=0.3 and 0.7, respectively. However, no retrograde temperature behavior for the T_p of the ω_1 peak was observed in the present experiment.

Peng and Dawson, [23,26] and Matsushita and Hansen[24,25] have stated that these ω peaks resemble those for nitrogen desorption (λ state) from an adsorbed layer of ammonia on tungsten heated to 800 K or from that of activated nitrogen by electron bombardment, and that the number of total nitrogen atoms adsorbed is 8.6×10^{14} atoms/cm^2 because one nitrogen atom occupies a single vacancy site. Since one nitrogen oxide molecule may occupy a single vacancy site, a nitrogen oxide monolayer of 8.8×10^{14} molecules/cm^2 agrees with 8.6×10^{14} sites/cm^2 in the λ state of nitrogen adsorption.

The processes of adsorption, dissociation and desorption may be expressed as follows:

$$NO_{(g)} \longrightarrow NO_{(a)} \quad (1)$$
$$NO_{(a)} \longrightarrow N_{(a)} + O_{(a)} \quad (2)$$
$$2N_{(a)} \longrightarrow N_{2(g)} \quad (3)$$

Equations 2 and 3 are the reactions during the heating process. It is believed that the rate of process 2 is faster than that of process 3, since the rate of nitrogen desorption is roughly proportional to θ^2.

3) Desorption of Nitrogen from a Nitrogen Layer on Tungsten: The desorption spectra for various coverages of nitrogen are shown in Fig. 7. For nitrogen adsorption on tungsten at room temperature, three states, α, β_1, and β_2, were found in the desorption spectrum as has

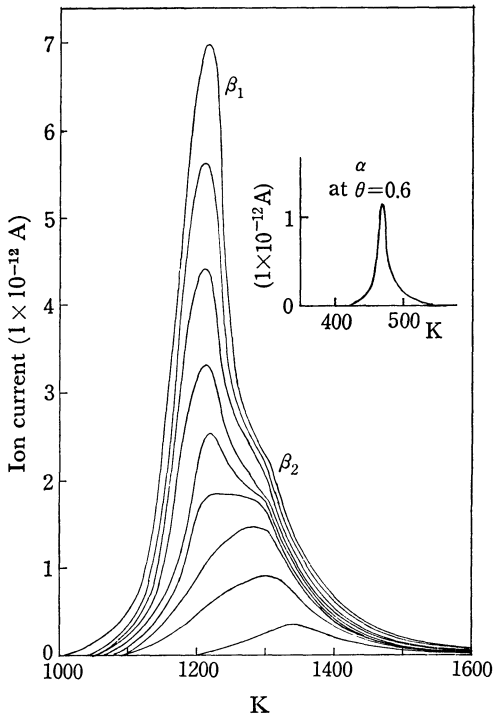

Fig. 7. The desorption spectra from various initial coverages of nitrogen.

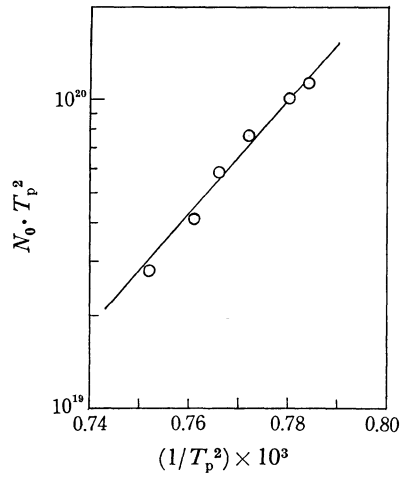

Fig. 8. A plot of log $N_0T_p^2$ *vs.* $1/T_p$.

been reported by other investigators.[16,17] The α state exhibits a maximum peak height (T_p: 470 K) at θ=0.6, and the α peak disappears for saturation coverage of nitrogen. The amount of α nitrogen desorbed corresponds to 5% of the β nitrogen at $\theta\simeq$0.6 (corresponding to 3% of a monolayer). Since the nitrogen from the α state desorbs at very low temperatures, it appears that the bond strength of W–$N_2(\alpha)$ is considerably weaker than those of the β states.

The β_1 peak appears beginning at $\theta\simeq$0.3. The T_p of the β_1 peak does not shift from the value of 1205 K as the coverage increases. According to Redhead's report,[27] and assuming that the desorption of the β_1 state follows first order kinetics and that the pre-exponential factor is 10^{13}/s, we obtain a value of 78 kcal/mol as the activation energy of β_1 nitrogen desorption.

On the other hand, the T_p of the β_2 peak shifts to a lower temperature with an increase in the coverage. Also, according to Redhead, when the desorption kinetics are 2nd order, the following equation should be valid:

$$E/RT_p^2 = (N_0\nu/\bar{\beta})\exp(-E/RT_p),$$

where N_0 is the initial coverage, ν is the rate constant, E is the activation energy for β_2 nitrogen desorption, and $\bar{\beta}$ is the rate at which the filament temperature is raised. A plot of $\log(N_0T_p^2)$ *vs.* $1/T_p$ is shown in Fig. 8. From the slope, the activation energy for desorption in the β_2 state is 80.5 kcal/mol. Data for the activation energy for nitrogen desorption on tungsten by other investigators are shown together in the Table 1.

References

1) J. A. Becker "Advances in Catalysis," Vol. 7, ed. by W. Frankenburg, V. I. Komarewsky, and K. E. Rideal, Academic Press, New York (1955), p. 135.
2) G. Ehrlich "Advances in Catalysis," Vol. 14, ed. by D. D. Eley, H. Pines, and P. B. Weisz, Academic Press, New York (1963), p. 255.
3) P. J. Estrap and E. G. McRae, *Surface Sci.*, **25**, 1 (1971).
4) C. C. Chang, *Surface Sci.*, **25**, 53 (1971).
5) T. E. Madey and J. T. Yates, Jr., *J. Vac. Sci. Technol.*, **8**, 525 (1971).
6) J. T. Yates, Jr. and T. E. Madey, *J. Chem. Phys.*, **45**,

1623 (1966).
7) J. T. Yates, Jr., T. E. Madey, and J. K. Payn, *Nuovo Cimento Suppl.*, **5**, 558 (1967).
8) T. E. Madey, J. T. Yates, Jr., and N. E. Erickson, *Surface Sci.*, **43**, 526 (1974).
9) R. Klein and J. T. Yates, Jr., "Proc. 2nd Internal. Conf. on Solid Surfaces," 1974, *Jpn. J. Appl. Phys.*, Suppl. 2, Pt. 2 (1974).
10) T. Tamura, *Bull. Chem. Soc. Jpn.*, **44**, 590 (1971).
11) T. Tamura, *Bull. Chem. Soc. Jpn.*, **44**, 2116 (1971).
12) G. Ehrlich, *J. Chem. Phys.*, **36**, 1171 (1962).
13) R. E. Schlier, *J. Appl. Phys.*, **29**, 1162 (1958).
14) G. Ehrlich, *J. Phys. Chem.*, **34**, 29 (1961).
15) T. W. Hickmott and G. Ehrlich, *J. Phys. Chem. Solids*, **5**, 47 (1958).
16) T. Oguri, *J. Phys. Soc. Jpn.*, **18**, 1280 (1963).
17) L. J. Rigby, *Can. J. Phys.*, **43**, 532 (1965).
18) J. T. Yates, Jr. and T. E. Madey, *J. Chem. Phys.*, **43**, 1055 (1965).
19) T. E. Madey and J. T. Yates, Jr., *J. Chem. Phys.*, **44**, 1675 (1966).
20) D. A. King and M. G. Wells, *Surface Sci.*, **29**, 454 (1972).
21) P. A. Redhead, *Trans. Faraday Soc.*, **57**, 641 (1961).
22) R. B. Heslop and P. L. Robinson, "Inorganic Chemistry," Elsevier Pub., Co., New York (1960), p. 319.
23) Y. K. Peng and P. T. Dawson, *J. Chem. Phys.*, **54**, 950 (1971).
24) K. Matsushita and R. S. Hansen, *J. Chem. Phys.*, **52**, 3619 (1969).
25) K. Matsushita and R. S. Hansen, *J. Chem. Phys.*, **52**, 4877 (1969).
26) P. T. Dawson and Y. K. Peng, *Surface Sci.*, **33**, 565 (1972).
27) P. A. Redhead, *Vacuum*, **12**, 203 (1962).