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Isotherm for Ni-O₂ Adsorption System

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The activation energy of dissociative adsorption of oxygen on polycrystalline nickel surface is calculated from adsorption isotherms obtained using X-ray photoelectron spectroscopy. Negative value of this activation energy (-5.9 kJ/mol) indicates that the adsorption takes place through an undissociated precursor state. An adsorption energy for this precursor state is calculated assuming the precursor state as a molecularly physisorbed state ($E_{ad} = -7.9$ kJ/mol). Finally, an adsorption isotherm equation is derived as a function of the gas exposure, which agrees with the experimental isotherms reasonably good.

Introduction

The adsorption of oxygen on Ni surface has been extensively studied in connection with oxidation of the metal, heterogeneous catalysis, and adsorption mechanism. According to the results reported so far¹⁻¹¹, oxygen is adsorbed dissociatively on Ni surface at the initial stage and forms NiO with the increase of the adsorption amount. There have been recent reports that oxygen is dissociatively adsorbed through a molecularly adsorbed precursor state when oxygen is adsorbed on the surface¹²⁻¹⁴. It is believed that the precursor state species is not experimentally detected at room temperature because of its short life time. It has been, however, confirmed experimentally that oxygen is molecularly adsorbed at low temperature^{15,16}.

In studying the interaction of the gas with the metal surface, it is meaningless to give the adsorbed amount of gas as a function of the gas pressure since the rate of desorption is negligibly shown in this adsorption system. At the initial stage of adsorption of oxygen on the Ni surface, the sticking coefficient is known to approach one¹⁷. Therefore it is much more useful to show the adsorbed amount as a function of the gas exposure. The adsorption of oxygen on metal surface is accompanied by complex reactions such as the diffusion of oxygen into the bulk, therefore it is not easy to interpret theoretically the adsorption isotherm. Benziger *et al.*¹⁸ derived an adsorption isotherm thermodynamically for diatomic molecules such as CO, NO and N₂ on transition metal surfaces. But this was not the adsorption isotherm which showed adsorbed amount as a function of oxygen exposure but an adsorption isobar which showed changes of adsorption

coverage as a function of temperature. The adsorption isobar predicted merely which was dominant adsorption between molecular adsorption and dissociative adsorption in terms of the magnitude of adsorption energy.

In this work, the activation energy of dissociative adsorption is calculated from the adsorption isotherms obtained using X-ray photoelectron spectroscopy and an adsorption isotherm of gaseous oxygen molecule as a function of oxygen exposure is derived theoretically. The adsorption energy of the precursor state, a parameter needed in the derivation, is calculated from pair-wise interaction energy on the assumption that the precursor state is a molecularly physisorbed state.

Theory

A. Apparent Activation Energy. The apparent activation energy of the dissociative adsorption of oxygen on Ni surface is calculated from an empirical adsorption isotherms obtained by Ahn, one of the author, *et al.*¹⁹ (Figure 1). Ahn *et al.* calculated previously the apparent activation energy assuming that the saturation coverage is in $c(2 \times 2)$ structure. However in this work the apparent activation energy is calculated without assuming any saturation coverage structure. The adsorption rate is obtained as a function of exposure from the slope of the adsorption isotherm, and then Arrhenius plots ($\ln\langle\text{rate}\rangle$ vs. $1/T$) at various oxygen exposures are made as shown in Figure 2. Finally the activation energy for an oxygen exposure is calculated from slopes of these Arrhenius plots, which is negative values.

The calculated activation energies plotted as a function of

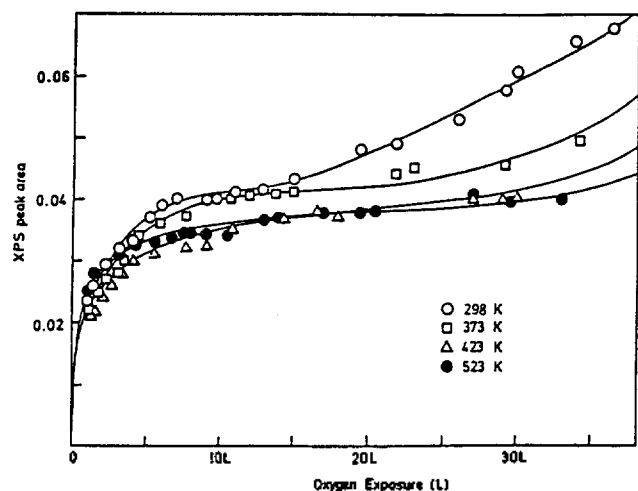


Figure 1. Isotherms of oxygen uptake at lower coverage on polycrystalline Ni surface at various temperatures. Solid lines are drawn to fit experimental values.

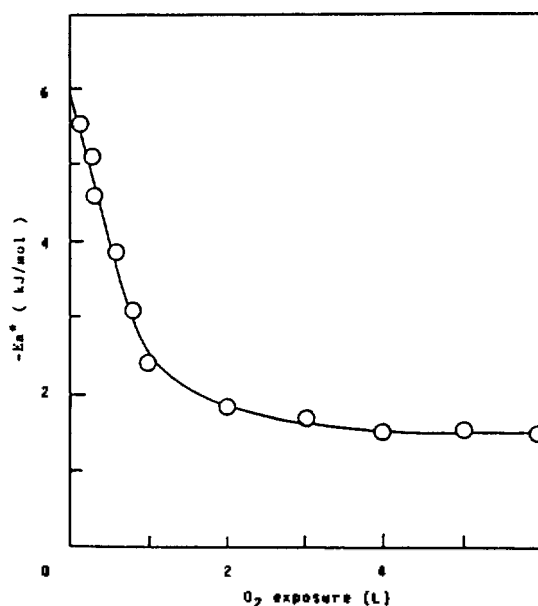


Figure 3. Activation energy of chemisorption as a function of oxygen exposure.

Table 1. Calculated Physisorption Energy of Oxygen Molecule on Nickel Surface

σ_{RR}	σ_{SS}	σ_{RS}	ϵ_{RS}	Z_{min}	E_{ad}
3.43	2.49	2.96	0.939	2.84	-7.9

length: Å, energy: kJ/mol

Steel's method²⁰, summing pair-wise interaction energies, by assuming that oxygen is physisorbed molecularly on Ni surface. Using the Lennard-Jones 12-6 potential for the pair-wise potential energy, the interaction energy between oxygen molecule and solid surface can be written as:

$$\frac{U_g(r)}{\epsilon_{RS}} = \frac{2\pi}{a_s} \sum_{\alpha} \left\{ s \left[\frac{2\sigma_{RS}^{12}}{5Z_{\alpha}^{10}} - \frac{\sigma_{RS}^6}{Z_{\alpha}^4} \right] + \sum_{g \neq \alpha} \sum_{k=1}^s \exp[ig(m_k + \gamma)] \right. \\ \left. \left[\frac{\sigma_{RS}^{12}}{30} \left(\frac{g}{2Z_{\alpha}} \right)^4 K_5(g, Z_{\alpha}) - 2\sigma_{RS} \left(\frac{g}{2Z_{\alpha}} \right)^2 K_2(g, Z_{\alpha}) \right] \right\} \quad (1)$$

where a_s is the area of a surface unit lattice cell, s is the number of atoms per unit lattice cell in the solid, Z_{α} is the vertical height between the gas molecule and the α th layer in the solid, γ is the two-dimensional vector parallel to the surface, g is the reciprocal vector and ϵ_{RS} is the depth of the interaction energy well. Here, ϵ_{RS} is set equal to ϵ_{RR}^{21} instead of taking a mean because ϵ_{SS} is so high as to give absurdly high contribution to the mean value of ϵ_{RS} [$\epsilon_{RS} = (\epsilon_{RR}^{21} \cdot \epsilon_{SS})^{1/2}$], and σ_{RS} is taken as an arithmetic mean of σ_{RR}^{21} and σ_{SS}^{22} .

For Ni-O₂ adsorption system the Ni(111) plane is taken as the most dominant surface^{23,25} on the polycrystalline Ni surface, and the 3 fold hole is considered as the one having the highest adsorption energy in the physisorption.

The calculated results and parametric values used therein are shown in Table 1. From the results, it can be said that in the adsorption model the oxygen is adsorbed molecularly at first and then rapidly dissociates through a transition state. The potential energy diagram based on the model is shown in Figure 4. As the adsorption energy of precursor

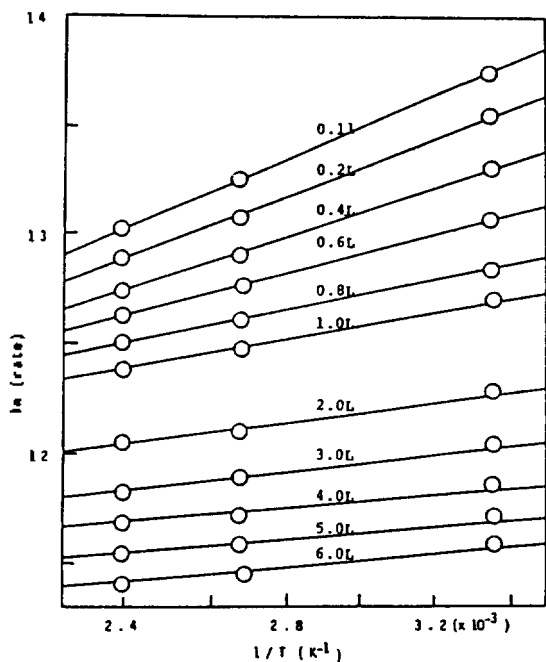


Figure 2. Arrhenius plots for dissociative oxygen adsorption at various exposures.

the oxygen exposure are shown in Figure 3. It is noted that the apparent activation energy increases as the oxygen exposure increases. It can be explained by the fact that as the oxygen exposure increases and as oxygen molecules adsorbed in the precursor state increase, the number of nonoccupied Ni sites decreases and the probability of the adsorbed oxygen molecules dissociate into atomic state decreases. The actual apparent activation energy for the adsorption of oxygen on polycrystalline Ni surface should be measured on a clean surface. This can be obtained by extrapolating the apparent activation energy to zero oxygen exposure. The value is -5.9 kJ/mol. The negative activation energy indicates the existence of undissociated precursor state.

B. Adsorption Energy of the Precursor State. The adsorption energy of the precursor state is calculated using

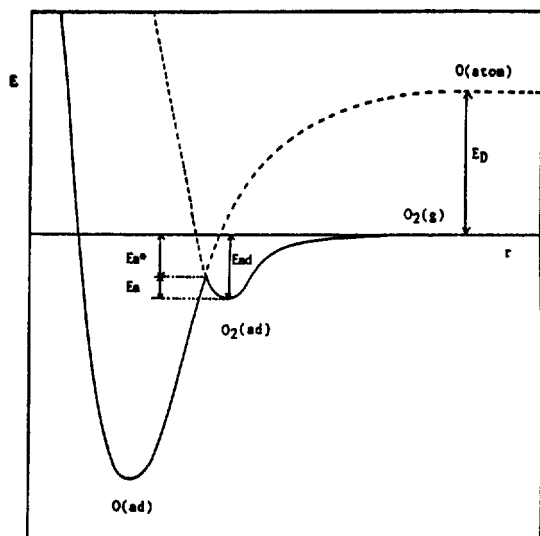


Figure 4. Potential energy diagram for Ni-O₂ adsorption system.

state, E_{ad} is -7.9 kJ/mol, and the apparent activation energy, E_a^* is -5.9 kJ/mol, actual activation energy is therefore about 2 kJ/mol.

C. Derivation of Adsorption Isotherm. The rate of oxygen adsorption on Ni surface can be written as following according to the activation complex theory²⁶:

$$r = x \frac{kT}{h} \exp(-\Delta G^*/RT) C_{O_2} C_{Ni} \quad (2)$$

where x is the transmission coefficient, ΔG^* is the activation free energy of adsorbed molecules transforming to transition state, C_{O_2} is the concentration of molecularly adsorbed oxygen on the surface, and C_{Ni} is the concentration of adsorption site on the surface. When the fraction of adsorption sites occupied by the precursor state molecules is written as θ' and the fraction of adsorbed oxygen in atomic state as θ , C_{O_2} is θ' and the concentration of nonoccupied adsorption site, C_{Ni} , is $(1 - \theta' - \theta)$. Then the above equation becomes as

$$r = m\theta' (1 - \theta' - \theta), \quad (3)$$

where

$$m = x \frac{kT}{h} \exp(-\Delta G^*/RT).$$

The concentration of the precursor state is calculated as following: The number of adsorbed oxygen in the molecular state is the number of molecules colliding with surface per unit time multiplied by mean life time of adsorbed molecules, accordingly the number of adsorbed oxygen molecules is

$$N_{O_2(ad)} = N(1 - \theta' - \theta) \tau \quad (4)$$

where N is the number of colliding molecules per unit area of the surface per unit time, and τ , the life time of adsorbed molecules, can be given according to Frenkel²⁷ as $\tau = \tau_o \exp(Q/RT)$. Here, τ_o is the time of oscillation of molecules in adsorbed state, and Q is the adsorption energy of precursor state. The fraction of site occupied by the precursor state can be obtained as following by introducing the number of collision N calculated with the gas kinetics theory^{28,29},

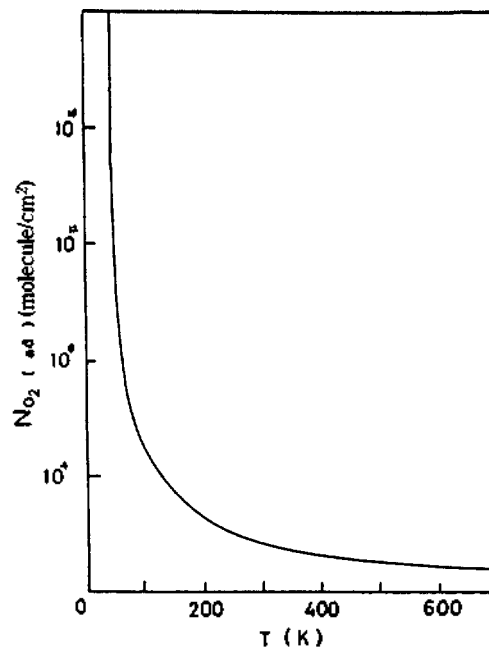


Figure 5. Number of adsorbed oxygen molecules calculated by using Frenkel equation as a function of temperature at 5×10^{-8} torr.

$$\theta' = KP(1 - \theta' - \theta) \quad (5)$$

where

$$K = \frac{A \exp(Q/RT)}{(2\pi MRT)^{1/2} N_o}$$

Here, A is Avogadro number, P is pressure of oxygen gas, M is molecular weight of oxygen, N_o is total number of adsorption sites per unit surface. By combining eq. (2) and (5), following equation can be obtained.

$$r = \frac{mKP(1 - \theta)^2}{(1 + KP)^2} \quad (6)$$

Meanwhile, the reaction rate can be given as the change of coverage with time. Therefore, above equation is written as

$$\frac{d\theta}{dt} = \frac{mKP(1 - \theta)^2}{(1 + KP)^2} \quad (7)$$

This equation is integrated with θ from 0 to θ and t from 0 to t , respectively, to give

$$\theta = \frac{mKL}{(1 + KP) + mKL} \quad (8)$$

This is the dissociative adsorption isotherm which shows the adsorbed amounts of gas on the solid adsorbents as a function of the gas exposure.

D. Comparison of the Isotherm with Experimental Results. In order to obtain a theoretical adsorption isotherm for Ni-O₂ adsorption system, the amount of molecularly adsorbed oxygen on Ni surface ($\sigma = n\tau$) are calculated at various temperatures (Figure 5). The number of molecularly adsorbed oxygen species calculated with the above isotherm is very low in agreement with experimental results. As in the Ni-O₂ system, in case, where the fraction of adsorbed molecules in precursor state is negligible, the term

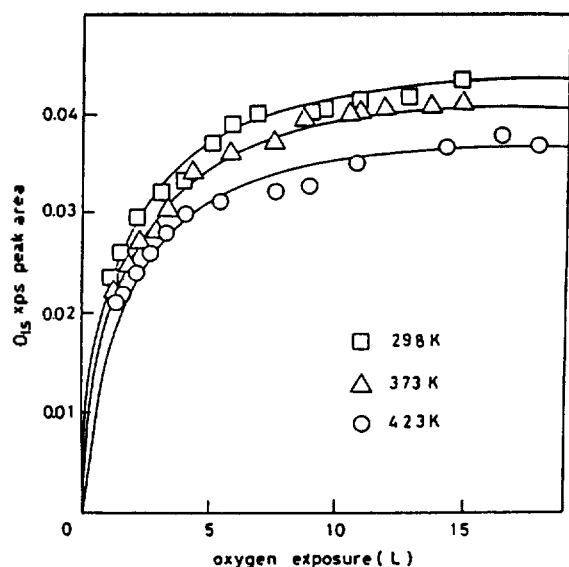


Figure 6. Isotherms of oxygen on polycrystalline Ni surface at various temperatures. Solid lines are those theoretically obtained.

Table 2. The Parameters Used for Ni-O₂ Adsorption System

Q (kJ/mol)	ΔG^* (kJ/mol)	τ_0 (sec)	α	N_0 (molecule/cm ²)
-7.9	5	10 ⁻¹³	1	1 × 10 ¹⁵

$KP (= \sigma/N_0)$ in the denominator can be neglected. Therefore, the adsorption isotherm for Ni-O₂ adsorption system can be simplified as follows

$$\theta = \frac{mKL}{1 + mKL} \quad (9)$$

Isotherms for adsorption of oxygen on polycrystalline Ni surface are calculated using eq. (9) at 298, 373, and 423K. The calculated isotherms along with experimental values are shown in Figure 6 and the parameters used in that calculation are shown in Table 2. The adsorption isotherm is parabolic.

Discussion

The adsorption isotherm which gives the adsorbed amount of gas as a function of the gas exposure is derived, assuming a model consistent with experimental evidence. The isotherm is parabolic, and coincides with experimental isotherms.

The values used for adjustable parameters are very reasonable; The energy of molecularly physisorbed precursor state is calculated. It is -7.9 kJ/mol which is very close to the heat of vaporization of the oxygen. The apparent activation energy obtained is very close to the value for W(100)-N₂ adsorption system (-7.0 kJ/mol) calculated by King *et al.*³⁰ and to the values for Pt-O₂ adsorption system (-4.2 kJ/mol and -3.3 kJ/mol) by Gland³¹ and White³². This low activation energy is considered to cause the dissociation of O₂ at the very moment of adsorption. In case where undissociated molecular adsorbed species are detected, the activation energy is found to be considerably high. For example, in Ni-CO

adsorption system where activation energy is 38.1 kJ/mol, it is found that undissociated CO species is detectable up to fairly high temperature.³³

The activation free energy of adsorbed molecules for the dissociation is given by $\Delta G^* = \Delta H^* - T\Delta S^*$, ΔH^* and ΔS^* being activation enthalpy and entropy, respectively. In this work, ΔH^* is 2 kJ/mol, which is very close to the value of 13 meV (1.25 kJ) obtained by Sayegan *et al.*^{15,16} for Ni(111)-O₂ adsorption system. ΔS^* is taken approximately -10J. The value is acceptable considering the fact that the oxygen is more or less mobile in the physisorbed state with small adsorption energy whereas in the transition state it is bound to the surface more tightly with a less mobility and accordingly with a decreased entropy.

It is very interesting to see that the number of adsorbed oxygen molecules in the precursor state rapidly increases as temperature goes down as shown in Figure 5. The parameter τ_0 is the time of oscillation of the molecules in adsorbed state and its value is taken usually as 10⁻¹³sec in physisorption. Total number of adsorption sites per unit surface, N_0 is taken as 10¹⁵ site/cm². This value is quite reasonable, considering the fact that the area of unit cell of polycrystalline Ni surface is about 10⁻¹⁵ cm² [(3.2Å)²].

According to the results obtained by Holloway *et al.*¹⁰ using AES and LEED, the oxygen molecules dissociatively adsorbed on Ni surface form p(2×2) structure at initial stage, and then change the structure into c(2×2) as the exposure is increased. The exposure at which this structure change takes place increases with the increasing temperature. This should be due to the decreasing rate of adsorption with the increasing temperature and agrees with experimental results of Ahn¹⁹, Mitchell⁸, Norton⁹ and Brundle¹¹. The results can be attributed to the fact that the life time of molecularly adsorbed species decreases with the increasing temperature, and as a consequence the probability of the dissociative adsorption decreases. The saturation coverages of the theoretical isotherms are adjusted to coincide with the experimental results.

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Preparation and Characterization of the L-prolino Co(III) Complexes with the Tetradentate N₂O₂-type Ligands

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Complexes of the type [Co(T)(L-pro)], where T is the quadridentate N₂O₂-type ligand, N,N'-dimethylethylenediamine-N,N'-diacetate or N,N'-dimethylethylenediamine-N,N'-di- α -butyrate, have been prepared. The complexes were separated into the two stereoisomers, Δ -*s-cis*-[Co(T)(L-pro)] and Λ -*s-cis*-[Co(T)(L-pro)]. They were characterized by their proton magnetic resonance, absorption and circular dichroism spectra, elemental analyses.

Introduction

In recent articles cobalt(III) complexes of the N,N'-dimethylethylenediamine-N,N'-diacetate (dmedda) have been obtained in the *s-cis* geometry only.¹⁻⁵ Jung *et al.* have synthesized the dmedba(N,N'-dimethylethylenediamine-N,N'-di- α -butyrate) ligand containing both the C-ethyl and N-methyl substitutions. The cobalt(III) complexes of the dmedba have been found also *s-cis* isomer only.⁶ The stereochemistry of cobalt(III) complexes with optically active amino acids is an interesting problem, and many studies have been directed toward the stereoselectivity or stereospecificity of those complexes.⁷⁻¹¹

Recently, the amino acid cobalt(III) complexes of dmedda ligand, [Co(dmedda(aa))], (aa = S-methyl-L-cysteinate, L-glutamate, L-aspartate, L-serinate) have been prepared from the reaction between the *s-cis*-[Co(dmedda)Cl₂]⁻ complex and the trifunctional amino acids. The trifunctional amino acids have shown remarkable stereospecificity in their coordination to the racemic *s-cis*-[Co(dmedda)Cl₂]⁻ giving the Δ -*s-cis*-[Co(dmedda(aa))] absolute racemic *s-cis*-[Co(dmedda)Cl₂]⁻ giving the Λ -*s-cis*-[Co(dmedda(aa))] absolute configuration only.⁵

In the present paper, some aspects of the stereochemistry of the [Co(T)(L-pro)] complexes are dealt with; T = dmedda, dmedba. It will be shown that the two stereoisomers, Δ -*s-cis*-[Co(T)(L-pro)] and Λ -*s-cis*-[Co(T)(L-pro)], are stereoselectively formed in the *s-cis*-cobalt(III) complexes of dmedda and dmedba.

Experimental

Physical Measurements. Electronic absorption spectra were obtained with a Shimadzu UV-240 Spectrophotometer. ¹H-NMR spectra were recorded on a varian EM 360L Spectrometer. Infrared spectra were taken with a Hitachi 270-30 Spectrophotometer. Elemental analyses were performed by Korea Advanced Institute of Science and Technology. Circular dichroism spectra were measured using a Jasco J-550 C Automatic Recording Spectropolarimeter.

Preparation of *s-cis*-Hydrogen(N,N'-dimethylethylenediamine-N,N'-di- α -butyrate) Dichloro Cobaltate (III), *s-cis*-H[Co(dmedba)Cl₂]. 2.0g of barium N,N'-dimethylethylenediamine-N,N'-di- α -butyrate⁶ was dissolved in 20 ml of water. 1.4g of cobaltous sulfate heptahydrate dissolved in 20 ml of water was added to this solution and the