THE ADSORPTION AND DECOMPOSITION OF N₂O ON NICKEL (100)

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The adsorption and decomposition of N_2O on clean and oxygen covered Ni(100) surfaces has been studied using a combination of Auger electron spectroscopy (AES) and molecular beam relaxation spectroscopy (MBRS) techniques. As observed in a previous study of this reaction on the Ni(110) surface, N_2O decomposes to yield N_2 gas and adsorbed O at temperatures between 200 and 800 K. Measurements at temperatures below 200 K led to the identification of two weakly adsorbed precursor species, one on clean surfaces and the other on surfaces covered with 0.25 ML of adsorbed O. The adsorption rate constants measured for these two species are consistent with values inferred indirectly in the previous study.

1. Introduction

In a previous study of the decomposition of N_2O on the Ni(110) surface [1], it was determined from the behavior of the reaction probability as a function of the extent of reaction that the reaction took place through the intermediation of one or more weakly bound precursor species. Direct information on the energetics of these precursor species could not be obtained, however, due to experimental limitations. In the present work we report the results of a similar study in which modifications to the experimental system permit direct measurement of the precursor adsorption and desorption kinetics.

We have studied the adsorption and decomposition of N_2O on the Ni(100) surface over the temperature range from 170 to 500 K using a combination of molecular beam relaxation spectroscopy (MBRS) and Auger electron spectroscopy (AES) techniques. The combination of the wide range of temperature with the two spectroscopic techniques has permitted us to determine independently the energetics of the various reaction steps involved.

2. Experimental

2.1. Apparatus

All experimental work was carried out in an all-metal ultrahigh vacuum system. A schematic top view of the system is shown in fig. 1. The sample, a

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Fig. 1. Schematic top view of experimental system.

Ni(100) single crystal disc 1 cm in diameter and 0.1 cm thick, was mounted on the axis of the system on a universal positioner. The sample was heated by electron bombardment from a shielded filament; its temperature was measured by a W-26%Re/W-5%Re thermocouple spot-welded to the edge of the crystal. The sample could be cooled by passing liquid nitrogen through a tube in intimate contact with the sample holder. The available temperature range was from 170 to 800 K.

 N_2O gas was introduced to the sample as a time-modulated molecular beam, using the differentially pumped molecular beam source shown at the left of fig. 1. The maximum beam intensity was roughly 10^{10} molecules/cm² s. The beam was square-wave modulated at frequencies from 20 to 200 Hz.

Product species desorbed from the surface following reaction, or unreacted reactant species, could be detected by the doubly differentially pumped quadrupole mass spectrometer positioned 90° away from the incident beam direction. The output from this mass spectrometer could be detected either with a two-phase lock-in amplifier or by a pulse counting preamplifier followed by a multichannel scaler to permit determination of the waveform of the scattered material.

The system was also equipped with a cylindrical mirror electron energy analyser for AES measurements, also at 90° to the incident beam direction, and an ion gun and argon gas supply for sample cleaning.

2.2. Procedures

Prior to kinetic studies, the sample was cleaned by repeated cycles of bombardment by 1000 eV argon ions and annealed at 800 K. Final traces of carbon were removed by titration with oxygen gas at 700 K. Following this treatment, Auger spectra of the surface showed only the expected peaks for nickel, plus a series of small peaks at 148, 178 and 220 eV. These peaks, which decreased rapidly with either heating or ion bombardment, are attributed to electron diffraction effects as first noted by Becker and Hagstrum [2]. Surface perfection was also monitored using the elastic peak of a scattered helium beam. The angular width of this peak is a sensitive function of both the cleanness of the surface and surface perfection. After extensive cleaning as described above, the angular width of the specular helium peak was less than 0.5°, the angular precision of the sample manipulator.

Because results of the previous study of N_2O decomposition on Ni(110) suggested the involvement of two distinct precursor species, on bare surface and oxygen covered sites respectively, an initial study was carried out to determine the conditions required to produce known and controlled surface oxygen coverages. In these studies, the sample was held at the desired temperature and exposed to a flux of N_2O or O_2 gas introduced through the molecular beam source. The net result of this exposure was in all cases the development of a surface oxygen coverage. The extent of this surface oxygen coverage was determined by Auger spectroscopy. In all cases the electron gun of the Auger spectrometer was turned off during the gas exposure to avoid artifacts associated with electron bombardment.

Exposure of the clean surface to O_2 produced the same results as observed previously for this same surface by Holloway and Hudson [3]. Exposure to a flux equivalent to 10^{-7} Torr at a temperature of 400 K for a few minutes led to the formation of 0.25 ML of adsorbed oxygen. Under these conditions the onset of oxide nucleation did not occur for a long time, and a controlled oxygen coverage could be obtained reproducibly. The saturation oxygen coverage obtained in this way was used as a calibration of the sensitivity of the Auger spectrometer. Exposure of the surface to O_2 fluxes equivalent to 10^{-6} Torr or greater led to the formation of a thin oxide layer, also as observed previously [3].

Results for the case of N_2O exposure are shown in fig. 2. At temperatures below about 200 K, on a clean, well ordered surface, the decomposition reaction is essentially completely suppressed, and the surface remains free of adsorbed oxygen for an extended period. As the temperature is increased, the extent of the decomposition reaction increases, reaching a final saturation above 670 K at an oxygen adlayer coverage of 0.25 ML. The previous study of this reaction on Ni(110) showed a similar saturation at 0.33 ML [1].

Similar exposure studies, carried out on surfaces that had been exposed to



Fig. 2. Saturation oxygen coverage resulting from long exposure of the Ni(100) surface to N_2O as a function of surface temperature.

bombardment by 500 eV argon ions at total doses as low as 1.4×10^{15} ions per cm², showed saturation oxygen coverages of 0.25 ML at all temperatures, indicating that, at least at low temperatures, the decomposition reaction takes place only at defect sites on the surface. Similar behavior was observed by Onchi and Farnsworth for this same system [4].

Mass spectrometric detection of the scattered gas flux during exposure of the surface to N_2O indicated that the only species desorbed were N_2 , arising from the decomposition process, and unreacted N_2O . In this work, and in the kinetic measurements described below, the scattered N_2O intensity was determined using the fragment ion peak at mass 30 rather than the parent peak at mass 44 in order to avoid interference from background CO_2 .

The major kinetic measurements made in this study were of the non-dissociative adsorption of N_2O on clean and oxygen-covered nickel surfaces. These measurements were made using two related types of MBRS technique. In all cases, the initial step was to prepare a surface that was either clean or covered with a predetermined amount of oxygen (0.25 ML or a thin oxide layer). In one set of experiments, the detector mass spectrometer was tuned to mass 30, to detect N_2O , and the output, sensed as pulses, sent to the input of the multichannel scaler. The multichannel scaler was triggered by a reference signal from the molecular beam chopper so as to collect the waveform of the scattered N_2O molecules. In the other set of experiments, the mass spectrometer output at mass 30 was detected by a two-phase lock-in amplifier. The in-phase and quadrature signals from the lock-in amplifier were sent to the xand y-channels of an x-y recorder. With the molecular beam on, and the sample at room temperature, the phase of the lock-in amplifier was set so as to maximize the in-phase signal. The sample was then cooled, and the lock-in signal monitored continuously. As the sample was cooled past the point at which the surface lifetime of the adsorbed N₂O became comparable to the beam modulation frequency, the resulting changes in the in-phase and quadrature signals were displayed on the x-y recorder, generating the reaction product vector (RPV) plot for the adsorption-desorption process directly.

3. Results and discussion

In this section, we will discuss separately the results of kinetic measurements on clean surfaces, surfaces covered with 0.25 ML of oxygen, and surfaces covered with a thin oxide layer. Finally, the results obtained will be discussed in terms of the previous study of N_2O decomposition on Ni(110) [1].

3.1. Clean nickel surfaces

The RPV plot obtained for N₂O scattering from the clean nickel surface at temperatures below that at which the decomposition reaction could take place is shown in fig. 3. The experimental data shown were derived from the x-y plots of signal phase and amplitude during cooling and heating. The RPV is defined in an MBRS experiment [5] as:

$\mathbf{RPV} = \boldsymbol{\epsilon} \, \exp(-\mathrm{i}\boldsymbol{\phi}),$

in which ϵ , the apparent reaction probability, and ϕ , the product phase lag,



Fig. 3. Reaction product vector plot for the exposure of the clean Ni(100) surface to N₂O at temperatures below 200 K. The solid line represents the behavior expected for a simple first-order desorption process.

depend on both the reaction mechanism and the rate constants of all reaction steps that influence the overall reaction rate. The semicircle drawn in fig. 3 represents the form of the reaction product vector plot expected for a simple first-order adsorption process. The trend of the experimental points in fig. 3, which shows increasing departure from the simple first-order curve with decreasing temperature and a limiting value of ϕ approaching 45°, is typical of those cases in which the rate is controlled partly by a first-order desorption process and partly by surface diffusion. The expressions for ϵ and ϕ for this case have been developed independently by Ullman and Madix [6] and by Chang and Weinberg [7] for the case of diffusion to a reaction zone at the perimeter of a circular spot. Ullman and Madix [6] also show that the results are similar for the case of diffusion to rows of linear steps. In the present work, application of the resulting equations is hampered by the fact that the data have a fairly high noise level, and by the fact that the temperature dependence of the surface diffusivity, D, and the desorption rate constant, k, enter the expressions for ϵ and ϕ in a complicated fashion. It is useful, however, to look at the high and low temperature limits expected for this case. At high temperature, where D is large, the expressions for ϵ and ϕ reduce essentially to the simple first-order case, and the temperature dependence is dominated by the temperature dependence of k. Conversely, at low temperature, for an experiment at constant modulation frequency, Ω , ϵ depends primarily on $D^{1/2}$. Making this approximation, the apparent reaction rate constant of the desorption process can be calculated from the data of fig. 3. This has been done using both the first-order relation between k and ϵ , namely

$$k = \Omega / \left[\left(\frac{a}{\epsilon} \right)^2 - 1 \right]^{1/2},$$

in which a is the initial adsorption probability, and the first-order relation between k and ϕ , namely

$$k = \Omega / \tan \phi$$
,

yielding the results shown in fig. 4. The results based on the relation between k and ϵ and the high temperature portion of the results based on the relation between k and ϕ yield the desorption rate constant

$$k = k_0 \exp(-E/RT),$$

in which E is the activation energy for desorption and k_0 is the frequency factor. The resulting values in this case are

$$k = 10^{12.3 \pm 3.2} \exp(-6240 \pm 350/RT),$$

based on a linear regression analysis of the data below 1000/T = 7.1. The low temperature portion of the results obtained from the phase lag measurements yields the activation energy for surface diffusion as approximately 2000



Fig. 4. Arrhenius plot of the effective first-order rate constant for the desorption of N_2O from clean Ni(100): \Box , from the RPV plot amplitude data; +, from the RPV plot phase lag data; from waveform data.

cal/mol. The preexponential term in D cannot be determined without additional information about the details of the surface morphology. It is not clear why the phase lag data should be more sensitive to surface diffusion effects than the amplitude data.

Consider next the data obtained from waveform measurements. Ideally, the waveforms obtained would be treated using a Fourier analysis technique [8] to generate the reaction product vector plot. In the present case, the signal-to-noise ratio was not high enough to permit use of this technique. Consequently, the results were analysed by assuming that the surface process was a simple first-order adsorption-desorption and fitting the decreasing side of the waveform curve to the relation

 $I(t) = I(0) \exp(-1/kt),$

where k is the desorption rate constant defined above and t is time. In the course of this process, the observed waveforms were corrected for time-of-flight and chopper duty cycle effects. The values of k determined in this way are also plotted in fig. 4. The results of the waveform measurements are consistent with the results obtained from the reaction product vector plot but show considerably greater scatter. This is probably due to temperature instability or surface contamination effects during the long exposure times (15 min to 1 h) required to generate the waveform.



Fig. 5. Reaction product vector plot for the exposure of a Ni(100) surface covered with 0.25 ML of oxygen to N_2O at temperatures below 200 K. The solid line represents the behavior expected for a simple first-order desorption process.

3.2. Nickel with 0.25 ML oxygen

The reaction product vector plot obtained for this case is shown in fig. 5, again with the semicircular plot expected for a simple first-order process included for reference. In this case, the experimental data are well represented



Fig. 6. Arrhenius plot of the effective first-order rate constant for the desorption of N_2O from a Ni(100) surface covered with 0.25 ML of oxygen; \Box , from the RPV plot amplitude data; +, from the RPV plot phase lag data; •, from waveform data.

by the first-order model. Values of k have been determined from these data, again in terms of relations between k and both the signal amplitude and the phase lag. The results are shown in fig. 6. Linear regression analysis leads to the expression for k for this case of

$$k = 10^{10.5 \pm 2.2} \exp(4750 \pm 260/RT).$$

The results of the analysis of waveform measurements carried out on surfaces covered with 0.25 ML of oxygen are also shown in fig. 6. In this case the results of the waveform measurements lie above those obtained from the RPV plot, and again show considerable scatter. Linear regression analysis of the waveform data yields

 $k = 10^{12.1} \exp(-5500/RT).$

Due to the scatter in the waveform measurements, we cannot determine whether this apparent difference in desorption energy is significant.

3.3. Nickel oxide covered surfaces

A typical reaction product vector plot for this case is given in fig. 7. In this case the experimental result is well described by the simple first-order curve. Although this behavior was typical of results on oxide covered surfaces, the results showed considerable scatter from run to run. The results of waveform measurements on similar surfaces also showed considerable scatter. The reason for this behavior is not known with certainty, but is most likely associated



Fig. 7. Reaction product vector plot for the exposure of a Ni(100) surface covered with a thin layer of NiO to N_2O at temperatures below 200 K. The solid line represents the behavior expected for a simple first-order desorption process.

with the fact that the thin oxide layer has a fine grained polycrystalline structure, and that repeated oxidations yielded significantly different defect concentrations. An average over all measurements made yielded

$$k = 10^{12.5 \pm 5.0} \exp(-7300 \pm 1000/RT).$$

3.4. Comparison with previous results

As mentioned at the outset, we have previously studied the decomposition of N_2O on the Ni(110) surface [1]. In this study, which also involved the use of molecular beam scattering, the absolute probability of the decomposition reaction was measured as a function of the surface temperature and the extent of reaction. The successive site model [9] was used to determine the reaction mechanism, with the results being well described by the reaction scheme

$$(N_{2}O)_{g} \xleftarrow{\alpha \cdot J}_{k_{d}} (N_{2}O)_{p} \xleftarrow{k_{t}}_{k_{r}} (N_{2})_{p} + (O)_{a}$$
$$(N_{2}O)_{p} \xleftarrow{k_{d}}_{k_{m}} (N_{2}O)_{p} + (O)_{a}$$

Application of the successive site model also led to values of the ratios

$$RT \ln(k_{\rm f}/k_{\rm d}) = E_{\rm d} - E_{\rm f} = 3700 \, {\rm cal/mol},$$

and

$$RT \ln(k'_{\rm d}/k_{\rm d}) = E_{\rm d} - E'_{\rm d} = 600 \text{ cal/mol.}$$

In the context of the present work, k_d is equivalent to k for the clean nickel surface and k'_d is equivalent to k on the surface covered with 0.25 ML of oxygen. If we insert the values of the desorption energies determined in the present work into the expressions developed previously, we determine that

$$E_{\rm d} = 6240 \, {\rm cal/mol},$$

 $E'_{\rm d} = 4750 \, {\rm cal/mol},$

yielding

 $E_{\rm d} - E_{\rm d}' = 1490 \text{ cal/mol},$

in qualitative agreement with the previous study. Finally, we may use

$$E_{\rm f} = E_{\rm d} - 3700$$

to obtain

$$E_{\rm f} = 2540 \, {\rm cal/mol.}$$

These results are shown graphically in fig. 8, a schematic potential energy diagram for the reacting system.



Fig. 8. Schematic potential energy diagram for the decomposition of N_2O on nickel, combining the results of ref. [1] with the results of the present study.

In the above treatment we have assumed that the energetics of precursor adsorption are identical on the Ni(100) and Ni(110) surfaces. This is clearly an approximation. However, in view of the weak adsorption forces involved and the overall similarity of the decomposition reaction behavior on the two surfaces the approximation should be good enough that the treatment given will provide some insight into the surface processes involved.

4. Summary

The adsorption and decomposition of N_2O on clean and oxygen covered Ni(100) surfaces has been studied using two forms of the MBRS technique. At temperatures below 200 K the decomposition reaction procedes only at surface defects. The extent of the reaction increases with increasing temperature above 200 K, reaching saturation at a surface oxygen coverage of 0.25 ML above 670 K.

Surface	Preexponential	Desorption energy (cal/mol)
Clean nickel	$10^{12.3 \pm 3.2}$	6240± 350
0.25 ML oxygen	$10^{10.5 \pm 2.2}$	4750 ± 260
Nickel oxide	$10^{12.5 \pm 5.0}$	7300 ± 1000

Table 1 Rate constants for N₂O precursor desorption

The existence of a molecularly adsorbed N_2O precursor species, suggested by the results of previous work [1], has been confirmed on all surfaces studied. Desorption rate constants for the precursor species from the surfaces studied, as determined by MBRS waveform measurements and RPV plots, are summarized in table 1.

Comparison of the results of this study with those of the previous study indicates that the rate constants determined here are in good agreement with those deduced previously by analysis of the overall rate of the decomposition reaction.

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