

ADSORPTION OF NITROGEN DIOXIDE ON POLYCRYSTALLINE GOLD

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The adsorption of nitrogen dioxide (NO_2) on a polycrystalline Au surface was studied by temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). Three desorption states due to chemisorbed NO_2 were observed using TPD, with desorption activation energies, E_d , of 11, 13, and 17 kcal/mol. The desorption energies reflect the heats of adsorption of NO_2 on the polycrystalline gold surface, since NO_2 adsorption is not an activated process. Desorption of physisorbed NO_2 from N_2O_4 multilayers was also seen at 130–140 K. The sticking probability of NO_2 at 120 K is independent of coverage indicating a strong influence of a precursor state in the adsorption kinetics. Vibrational spectra using HREELS show that chemisorbed NO_2 is molecularly adsorbed on the surface, probably as a Au O,O'-nitrito surface chelate. No evidence for the dissociation of NO_2 on Au was found using AES, TPD, or HREELS, even for large exposures of NO_2 at surface temperatures up to 500 K. Comparison of these results with those for NO_2 adsorption on a Au(111) surface is made. High energy sites, such as steps and kinks, and other crystal faces of Au can chemically bond NO_2 more tightly than occurs on Au(111), but the activation energy for dissociation of NO_2 at all of these sites exceeds 17 kcal/mol, and thus NO_2 adsorption is reversible on Au under low pressure conditions.

1. Introduction

Our interest in understanding the interaction of gases with gold surfaces is motivated, in part, by several practical applications of gold catalysts and by observations of selective oxidation reactions occurring over gold surfaces. A number of studies have recently been published that are related to the development of Au thin film sensors for detection of hazardous gases [1]. Also, a tremendous impact is now being felt on measurements in the atmosphere for sensitive detection of NO_y (NO_x , and RNO_2 , where R is a radical group) by a

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process utilizing gold tubes to catalyze the reduction of higher nitrogen oxides using excess CO to produce NO which is then detected at extremely low levels by a chemiluminescence detector [2,3]. A similar reaction and catalyst was used in a commercial redox chemiluminescence detector for chromatography, in which excess NO₂ is reacted with chromatographic effluent over a gold catalyst to produce NO (detected by a chemiluminescence method) if the other reactant, i.e. the effluent, can be oxidized or oxidatively dehydrogenated [4–6]. Gold catalysts have been known to carry out selective oxidation reactions. For example, propylene can be oxidized to acrolein by reacting it in the presence of O₂ over a gold catalyst [7]. Also, gold in the presence of O₂ catalyzes the general reactions of oxidative dehydrogenation of monohydric alcohols to form the corresponding aldehydes and ketones [8] and also of ethylpyridines to the corresponding vinylpyridines [9]. Very selective oxidation reactions of hydrocarbons have also been reported in the presence of a gold catalyst using NO₂ as the oxidant [4].

In this letter, we report results of the adsorption and reaction of NO₂ on a polycrystalline Au surface using AES, TPD, and HREELS. This extends previous work on this system by Brundle and Carley [10] that dealt only with physisorption and complements our previous studies of the reaction of NO₂ on the Au(111) surface [11]. On Au(111), we found a surprisingly strong chemisorption bond of 14 kcal/mol. The bonding geometry of this species was determined to be an O,O'-nitrito chelating species with C_{2v} symmetry, using HREELS data and comparing it to IR data from transition metal complexes. No dissociation was observed under UHV conditions. Our new results for NO₂ adsorption on polycrystalline Au surfaces will be compared to results from single crystal gold [11,12] and silver [13] surfaces. The study of the reactions of NO₂ on noble metal surfaces is a topic of current interest in our laboratory [14–19].

2. Experimental

The experiments were conducted in a UHV chamber that has been described in detail previously [20]. The system was equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and a directed beam gas doser [14]. The polycrystalline gold foil (1.5 cm × 1.5 cm, 0.1 mm thickness, 99.998% purity) was heated resistively and cooled by direct contact with a liquid nitrogen reservoir. The sample was cleaned by argon ion sputtering at 800 K for six hours followed by exposure at 800 K to 1 × 10⁻⁸ Torr NO₂ for five minutes. This treatment resulted in a surface that was free from contamination according to AES. Details concerning the synthesis and purification of the NO₂ have been given previously [14].

A heating rate of 8.5 K/s was used in the TPD experiments. No signals were detected during these experiments except from masses 14 (N), 30 (NO), and 46

(NO₂). The N and NO signals in TPD matched the desorption profile of NO₂ in all cases with the intensity expected for cracking of NO₂ in the mass spectrometer ionizer. All HREELS spectra were taken in the specular direction ($\theta_{\text{in}} = \theta_{\text{out}} = 65^\circ$ from the sample normal) with a typical count rate of 1 kcps and 100 cm⁻¹ FWHM for the elastic peak on the polycrystalline surface.

3. Results and discussion

The NO₂ thermal desorption spectra following NO₂ exposures on Au(poly) at 120 K are shown in fig. 1. NO₂ desorbs from three chemisorbed states, denoted as β_3 , β_2 , and β_1 , with peak temperatures of 280, 220, and 180 K. The activation energies for desorption from these states are estimated to be 17, 13, and 11 kcal

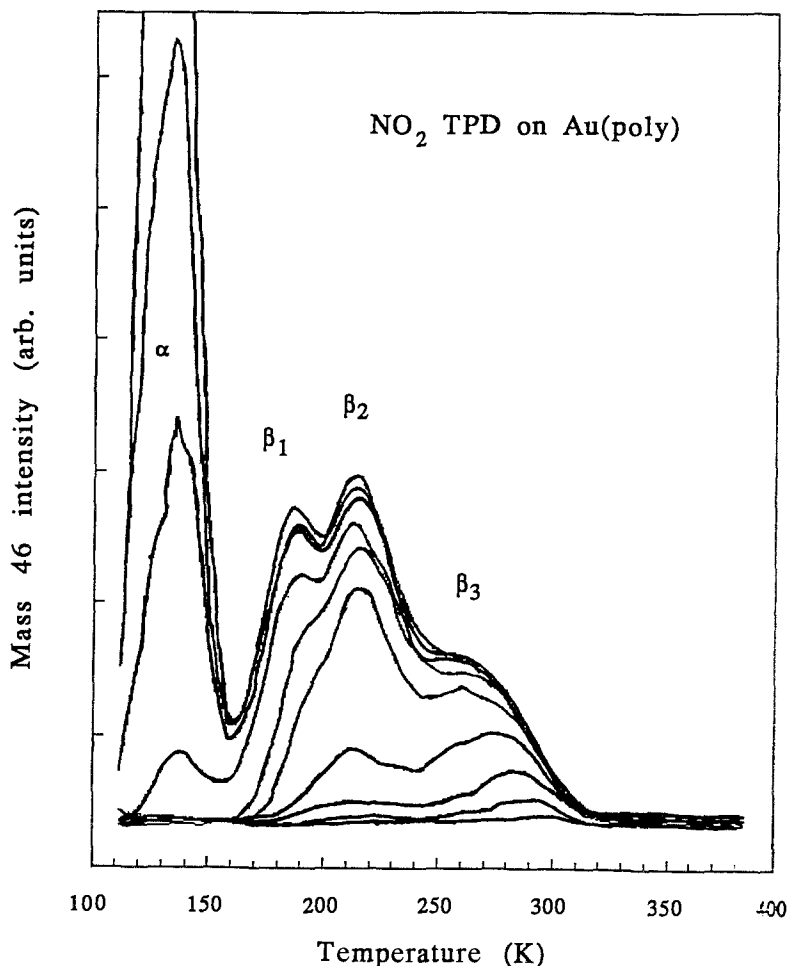


Fig. 1. NO₂ TPD spectra as a function of NO₂ exposure to Au at 120 K.

mole⁻¹, respectively. These activation energies were obtained by using Redhead analysis [22] and assuming first-order desorption kinetics and a pre-exponential factor of 10¹³ s⁻¹. Following larger exposures of NO₂, an additional desorption peak appears at 135 K, and eventually a state appears with zero-order desorption kinetics and an onset near 120 K. We have assigned these NO₂ TPD features as due to the decomposition of a physisorbed N₂O₄ multilayer. Desorption of NO₂ at these temperatures has also been observed in previous studies of NO₂ on several metal surfaces [11,14,16,19] and assigned to desorption from multilayers of N₂O₄.

During these TPD studies, no peaks corresponding to NO, O₂, or N₂ (other than those expected from NO₂ cracking in the mass spectrometer) were observed, showing that NO₂ decomposition does not occur on the polycrystalline Au surface under UHV conditions. Au surfaces that were sputtered at 120 K, without any subsequent annealing, were also exposed to NO₂; decomposition did not occur during TPD. We can estimate from our TPD results that 17 kcal/mol is a lower limit for the activation energy for NO₂ decomposition on Au. In addition, no evidence of decomposition of NO₂ was observed when the Au surface temperature was increased up to 500 K during NO₂ exposure. Finally, no increase in NO₂ adsorption was observed as the exposure temperature was increased. This indicates that NO₂ chemisorption is not an activated process (to any appreciable extent) on gold surfaces.

The adsorption/desorption behavior of NO₂ on Au(poly) can be compared to previous studies of the adsorption of NO₂ on an Au(111) surface [11]. For chemisorbed NO₂, Bartram et al. observed a single desorption peak between 220 to 230 K, depending on the coverage of NO₂. This is the same peak temperature that was seen for desorption from the β_2 state in our data, however, we did not observe a shift in peak temperature with NO₂ coverage. Bartram et al., also observed non-activated adsorption and did not detect any NO₂ decomposition on the Au(111) surface. A lower limit for the decomposition activation energy for NO₂ on Au(111) was estimated to be 25 kcal/mol.

Fig. 2 shows the adsorption uptake of NO₂ on Au(poly) at 120 K as measured by the integration of the NO₂ TPD peaks as a function of NO₂ exposure. Since the TPD area is proportional to coverage, the slope of the uptake curve is proportional to the NO₂ sticking probability. At high NO₂ exposures, this slope is proportional to the sticking coefficient for condensation into the N₂O₄ multilayer. The constant slope has been observed previously [11,14,15,22] and has been shown to correspond to a sticking coefficient of unity [14]. Fig. 2 shows that the slope at high exposures is equal to that observed at low exposures and, therefore, the initial sticking coefficient of NO₂ on the polycrystalline gold surface at 120 K is also near unity. These results agree well with the previous study of NO₂ on Au(111) [11].

Fig. 3 shows the vibrational spectra of several coverages of NO₂ adsorbed on the polycrystalline gold surface. These spectra were obtained using HREELS.

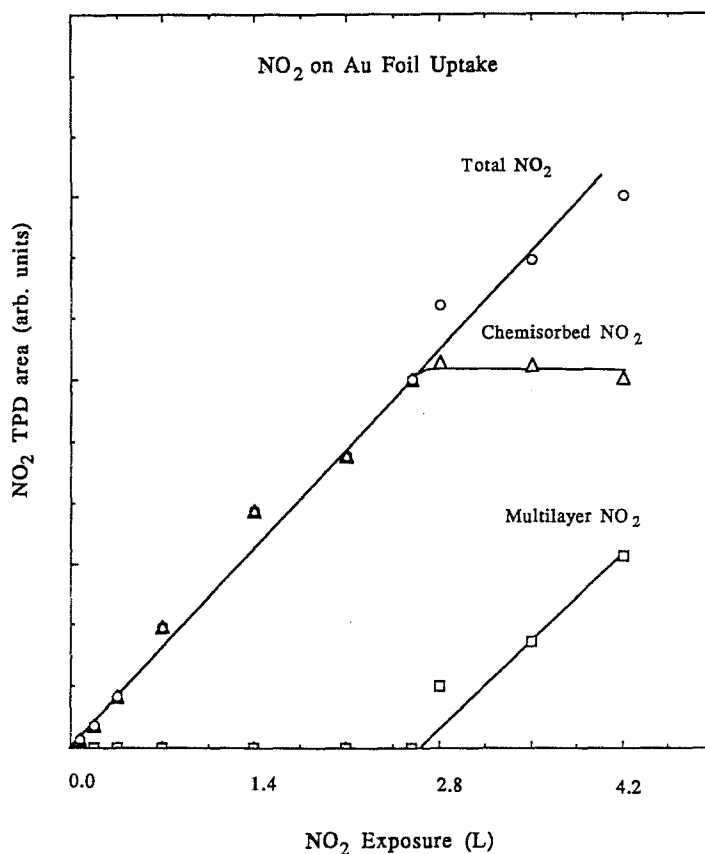


Fig. 2. Total coverage of NO₂ (○), chemisorbed NO₂ (Δ), and physisorbed NO₂ (□), as determined from the TPD data of fig. 1, as a function of NO₂ exposure to Au at 120 K.

This technique is normally used for single crystal metal surfaces, but it can be used for polycrystalline samples, albeit at a much reduced signal intensity. On a polycrystalline surface, multiple specular beams from various orientations of small facets cause a diffuse dipole scattering intensity (since dipole scattering is peaked around the specular scattering angle). This weak dipole scattering intensity cannot be easily distinguished from non-dipole scattering. Since the adsorption symmetry of a molecule is deduced by determining which vibrational modes in the molecule appear in dipole scattering [23], the HREELS spectra from polycrystalline surfaces cannot be used to assign the symmetry of the adsorption complex, but can be used to accurately measure vibrational frequencies. Fig. 3a shows the HREELS spectrum obtained from a N₂O₄ multilayer (as detected with TPD) on Au at 120 K. Three energy loss peaks are seen at 760, 1285, and 1745 cm⁻¹, with an intensity ratio of approximately 3:2:1. The frequencies and relative intensities of these peaks for N₂O₄ are in good agreement with work on Au(111) [11] and other metals [14,16,22]. The loss peaks are assigned to the NO₂

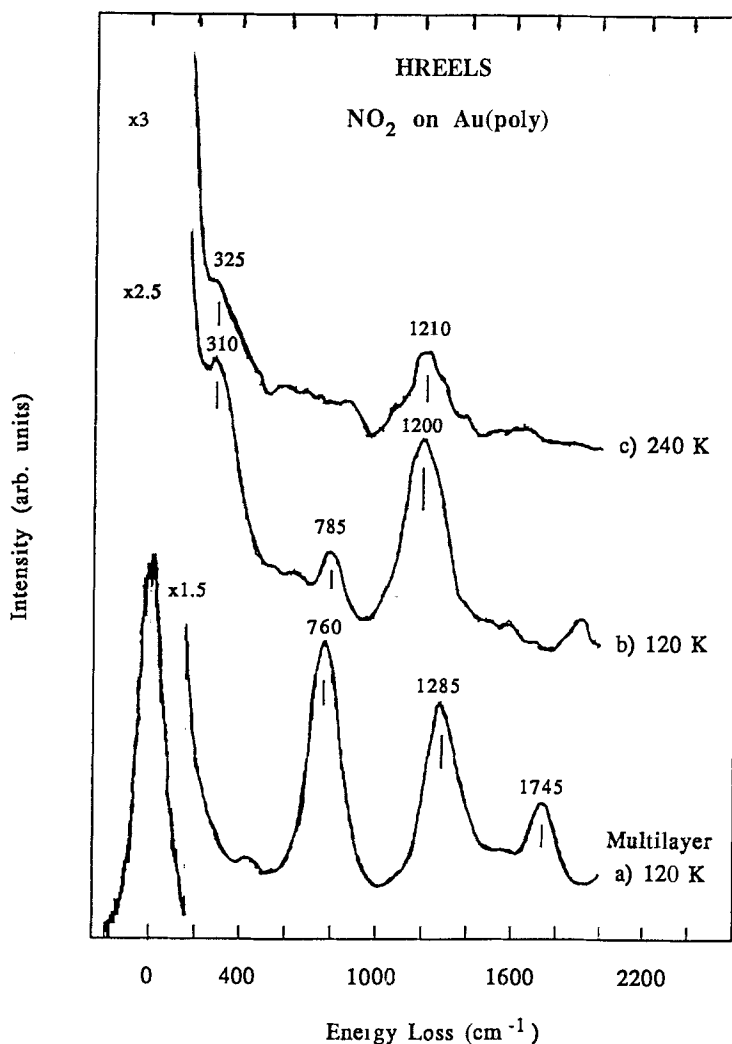


Fig. 3. HREELS spectra for three different NO_2 coverages on Au: a) physisorbed multilayer of NO_2 ; b) saturation coverage of a chemisorbed layer of NO_2 at 120 K; and c) a chemisorbed NO_2 layer after heating to 240 K.

bend, and the symmetric and asymmetric NO_2 stretching modes of N_2O_4 , respectively.

Fig. 3b shows the spectrum obtained for a saturation coverage of chemisorbed NO_2 on Au at 120 K. Four energy loss peaks are seen at 310, 785, 1200, and 1905 cm^{-1} . The assignment of these peaks can be made by comparison to the work of Bartram et al. [11] on Au(111). They observed peaks at 800 and 1180 cm^{-1} , and assigned these peaks to the NO_2 bend and the symmetric NO_2 stretch modes, respectively, of a O,O'-nitrito surface chelate (chemisorbed NO_2 bonded to the

surface through both oxygen atoms) with C_{2v} symmetry. They also observed the formation of N₂O₃ by radical addition of the surface chelate to NO, which caused intense HREELS peaks at 250 and 1890 cm⁻¹. The vibrational spectrum observed for chemisorbed NO₂ on polycrystalline Au indicates that NO₂ is chemisorbed on the polycrystalline surface in a similar geometry as that observed on the Au(111) surface, and that some small amount of N₂O₃ is formed at 120 K by reaction with NO in the background during the HREELS scan (NO is present at elevated levels in the chamber because of NO₂ decomposition on the walls and filaments). Simple NO coadsorption can be ruled out as a possible explanation of the 1890 cm⁻¹ peak since we observed no NO adsorption on clean polycrystalline Au at 120 K.

An unambiguous assignment of the NO₂ adsorption geometry cannot be made, yet several considerations support our conclusion that a O,O'-nitrito surface chelate is formed. It is clear that the vibrational spectrum of the chemisorbed NO₂ is indicative of a nearly symmetric coordination through either the nitrogen atom or the two oxygen atoms. This is evident from the lack of a high frequency asymmetric NO₂ stretching mode (at 1560 cm⁻¹ on Pt(111) [14]) that would occur if coordination occurred through both the nitrogen atom and an oxygen atom. The peak at 1200 cm⁻¹ on polycrystalline Au is only 20 cm⁻¹ higher than the symmetric NO₂ stretching mode observed at 1180 cm⁻¹ on Au(111), but is 70 and 100 cm⁻¹ lower than the peaks at 1270 and 1300 cm⁻¹ observed for the symmetric NO₂ stretch for the nitro (N-bonded) species on oxygen-covered Pt(111) [15] and Ru(001) [22] so that this bonding geometry is not likely to be present. The large width of the peak at 1200 cm⁻¹ is not simply the result of observing both the symmetric and asymmetric NO₂ stretching mode of a single O,O'-nitrito species with C_{2v} symmetry, based on off-specular observations reported on Au(111) [11]. The breadth of this peak could have two explanations. First, several C_{2v} O,O'-nitrito species with slightly different NO₂ stretching frequencies could be formed on the several different low Miller index planes of Au and on higher energy defect sites. Secondly, similar O,O'-nitrito species could be formed, but with lower symmetry than C_{2v} , e.g. C_s . Some insight into the frequencies expected for these modes comes from studies of N₂O₃ adsorbed on Au(111), where the symmetric and asymmetric NO₂ stretching modes are at 1180 and 1270 cm⁻¹, respectively. The broad loss peak centered at 1200 cm⁻¹ in fig. 3 is certainly consistent with this size of splitting of the stretching modes. The clear observation of N₂O₃ formation provides additional support for the O,O'-nitrito species. The lack of decomposition of NO₂ is also consistent with the assignment of the chelating adsorption geometry, since it has been suggested [14-17,19,22] that the μ -N,O nitrito species is the precursor required for decomposition.

The spectrum for chemisorbed NO₂ after heating to 240 K, shown in fig. 3c, is not significantly different from that in fig. 3b. The main difference is the disappearance of the N₂O₃-derived features. This indicates that there is no

significant change in the chemical nature of the chemisorbed NO₂ from high to low coverages and that the chelating geometry predominates.

Since these results can be explained by the presence of only a single NO₂ bonding geometry, the three desorption states observed in fig. 1 must be due to slightly different strengths of bonding interactions. The β_2 desorption state has a peak temperature similar to the desorption state of NO₂ from Au(111) [11]. Since the (111) face is the most thermodynamically stable, it is reasonable that it should also be found on the polycrystalline surface. Also, less stable (lower Au coordination number) crystal faces and defect sites such as edges, steps, and kinks should also be present. Thus, we attribute desorption from the β_1 and β_3 states as due to NO₂ bonded to sites on other crystal faces or other high energy sites present on the polycrystalline surface. Since decomposition was never observed in any of the NO₂ experiments here, we predict that the more reactive faces of Au single crystals will have little reactivity for NO₂ decomposition. We plan to study the adsorption and reaction of NO₂ on Au(331) and (110) surfaces to verify these predictions.

The reactivity of NO₂ on Au(111) [11] and Ag(110) [13] surfaces is quite different. NO₂ dissociates on Ag(110) at 100 K to form a coadsorbed layer of NO_(a) and O_(a). We suggest that this reactivity, compared to Au(111), is due to the inherent reactivity difference between Ag and Au, rather than the difference in reactivity inherent to the (110) versus the (111) faces of fcc metals. This comes from our lack of observation of any NO₂ decomposition on the polycrystalline Au surface, which must also contain some (110) facets. We plan experiments on the Ag(111) surface to check this hypothesis.

Finally, we would like to briefly discuss some of the relevance of these results to heterogeneous catalysis. Observation of strongly chemisorbed NO₂ (up to 18 kcal/mol) forces a fair consideration of bimolecular reaction mechanisms for oxidation reactions involving NO₂. The chelating NO₂ species has radical character and undergoes radical addition of NO to form N₂O₃. Thus, chelating NO₂ could undergo some very interesting reactions with other oxidizable reactants. The kinetic barrier to NO₂ dissociation ($E_a \geq 17$ kcal/mole) can be overcome at high NO₂ pressures and the role of NO₂ in oxidation catalysis could be to serve as a labile source of adsorbed oxygen atoms on Au. We have shown in other work [24] that oxygen atoms react rapidly at low temperatures to oxidize CO to CO₂. NO₂ is much easier to dissociate on Au than O₂ due to the formation of a strongly bound chemisorbed state of NO₂ and the weak ON–O bond (73 kcal/mol in the gas phase) compared to the O–O bond in O₂(g) (119 kcal/mol). Promoters for NO₂ reactions on Au could be used to alter the bonding geometry of adsorbed NO₂ or to enhance dissociative adsorption and hence influence the reactivity of NO₂. Also, lowering the temperature for the production of labile surface oxygen atoms could lead to increased catalytic selectivity for partial oxidation of hydrocarbons.

4. Conclusions

(1) Three desorption states for chemisorbed NO₂ are observed, with desorption activation energies of 11, 13, and 17 kcal/mol. These desorption energies reflect the heats of adsorption of NO₂ on different sites and crystal faces that comprise the polycrystalline gold surface.

(2) Vibrational spectra using HREELS show that NO₂ is molecularly adsorbed on the surface at all coverages of the chemisorbed states, probably as a Au O,O'-nitrito surface chelate bonded to the surface through both oxygen atoms.

(3) No evidence for the dissociation of NO₂ on polycrystalline gold was found using AES, TPD, or HREELS, even for large exposures of NO₂ at surface temperatures up to 500 K. We estimate that the activation energy for dissociation of NO₂ on Au surfaces exceeds 17 kcal/mol.

Acknowledgments

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