The Chemisorption of Nitric Oxide and Nitrogen on Rhenium

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The chemisorption of nitric oxide and nitrogen on a polycrystalline rhenium filament was studied using flash-desorption mass spectroscopy. For the chemisorption of nitric oxide, the initial sticking probability was found to be close to unity, with a saturation coverage of 5.2×10^{14} molecules/cm^2 at room temperature. Nitric oxide adsorbs nondissociatively, and dissociation occurs at an elevated temperature. The rate of the desorption of nitrogen from the nitric oxide layer is roughly proportional to θ^2. The majority of the oxygen in the nitric oxide layer was presumed to be liberated as rhenium oxide. The nitrogen adsorption was investigated in order to compare it with the nitric oxide adsorption. The saturation coverage and the initial sticking probability were 1.08×10^{14} molecules/cm^2 and 0.003 respectively.

Studies of the chemisorption of gases on metal surfaces are useful in deducing the mechanism of chemical reactions between gas and metal. Many studies in this field have been reported, and, recently, more useful information has been provided by such modern techniques as the method of flash filament, isotopic mixing, F.E.M., F.I.M., and L.E.E.D.1—3)

Extensive studies of the chemisorption of gases on tungsten have been made,4—19) but there have been only a few studies of rhenium.20—26)

Although there is a general similarity between the physical properties of tungsten and rhenium, particularly in their very high melting points, there are some marked differences in their chemical properties;27) for example, tungsten can form stable carbides and nitrides, while rhenium can not.

It is of interest to determine whether or not chemisorbed nitric oxide molecules are dissociated to form adsorbed atomic species, and what changes occur by flash desorption.

In the present investigations, the chemisorption of nitric oxide on rhenium has been studied using flash desorption mass spectroscopy. The saturation coverage of nitric oxide on rhenium was about one-third of that on tungsten, but the initial sticking probability was very high compared with that of other gases (its value was close to unity). The desorption of nitric oxide as molecules was negligibly small; the majority of the nitric oxide was decomposed and evaporated as nitrogen, oxygen, and rhenium oxide molecules when the rhenium temperature was raised.

Apparatus

The apparatus is shown schematically in Fig. 1. The reaction system, including the omegatron mass spectrometer, the Bayard-Alpert ionization gauge (B–A gauge), and the Pirani gauge, was all made of glass. The reaction vessel with a volume of $V=0.8\,l$ contained a rhenium filament with a geometrical area of $A=0.6$ cm^2. The rhenium filament was analyzed spectroscopically. (Found; Si:0.02%, Fe:0.008%, Mg:0.005%.) The system was pumped through a greaseless valve with an ion pump. After a rigorous outgassing of all parts of the system, the ultimate pressure, as read with the B–A gauge, was 3×10^{-10} Torr. The omegatron mass spectrometer was operated in a magnetic field of 3600G with a variable r. f. generator driven by a synchronous motor. The ion currents were measured with a high-sensitivity electrometer (TAKEDA RIKEN TR-81). The mass spectrum was recorded on a chart recorder with a 0.8 sec full-scale response. Under the conditions employed, the 28—30 masses were completely resolved, the sensitivities were taken to be 12 Torr^{-1} for N_2 (mass 28) and 11.8 Torr^{-1} for NO (mass 30). The omegatron was also used to measure the partial pressure as a function of the time in slow-flash experiments. This was done by recording the

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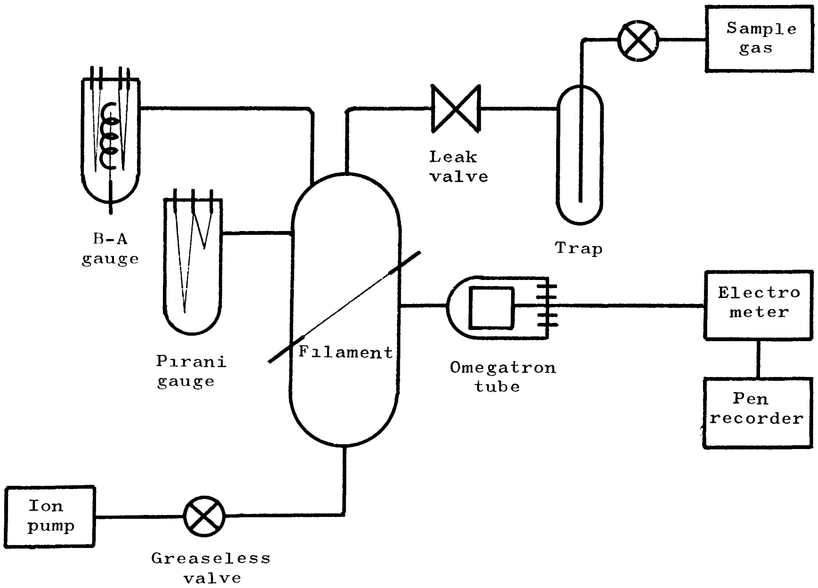

Fig. 1. Schematic drawing of the apparatus for flash desorption mass spectroscopy.

time variation of the ion current at a constant r.f. corresponding to a particular mass peak.

The Pirani gauge was used to measure the total pressure; it has a sensitivity of 7.2×10^{-8} Torr/μV for N_2 and NO. The B–A gauge was used only to measure the ultimate pressure; it was not operated during the actual experiments.

The rhenium filament could be flashed rapidly (within 1 sec) to 2200°K for rapid desorption experiments or slowly to 2000°K, with an approximately linear sweep rate of 20°/sec, for slow desorption experiments, by means of a controllable DC power supply. The temperature of the filament was determined from the resistance using the published values of the resistance-temperature relationship for rhenium,[28] above 1000°K, its temperature was also measured with a micro optical pyrometer.

The nitric oxide was prepared by dropping sulfuric acid into a mixed solution of potassium nitrate and potassium iodide. The gas thus evolved was passed through a concentrated caustic potash solution and a dry ice trap, was purified by liquid nitrogen trap-to-trap distillations, and was finally stored in a 1 *l* gas reservoir.

The nitrogen was prepared by the thermal decomposition of barium azide, labeled extra pure, and was introduced into a gas reservoir through the liquid nitrogen trap and stored there without further purification. No impurities up to mass 200 were detected by means of the omegatron mass spectrometer.

Procedure

Amount of Adsorption. In order to burn off any possible carbonaceous surface contamination prior to the adsorption experiments, the rhenium filament was heated to about 2000°K in oxygen of 1×10^{-6} Torr for several hours. When the rhenium filament is heated at high temperature in a nitric oxide atmosphere, rhenium oxide is formed on the surface. Therefore, the conventional flash-filament method[1,2,5,10] can not be used. To avoid this difficulty, the rhenium filament was flashed in a vacuum to clean it and then allowed to cool to room temperature. The leak-valve was opened to give a suitable exposure of the nitric oxide, and the pressure was recorded, by means of the omegatron or Pirani gauge, as a function of the exposure time. The number of nitric oxide molecules that strike the filament during the exposure can be calculated from the pressure-*vs*.-time curve. After the leak-valve was closed, the system was evacuated until the nitric oxide pressure dropped to 5×10^{-9} Torr. The system was then separated from the evacuating system by means of the greaseless valve, and the rhenium filament was flashed at 2200°K in the closed system. The amount of molecules desorbed can be calculated from the pressure and the volume of the system. In the case of the adsorption of nitric oxide, the number of molecules adsorbed is twice the number of molecules desorbed, because the desorbed gas is nitrogen.

Desorption Spectra. Nitric oxide or nitrogen, at a desired pressure, was streamed over the rhenium filament by adjusting the leak-valve. After the desired exposure time had passed, the leak-valve was closed and the system was evacuated. When the pressure dropped to 5×10^{-9} Torr, the slow desorption runs were initiated by using a controllable DC power supply. At that time, ion currents of the omegatron mass spectrometer for each mass were recorded on the chart recorder as a function of the time. The desorption spectra were obtained for each chemical species; they are shown in Fig. 6.

Results and Discussion

Sticking Probability and Amount of Adsorption. The number of molecules of nitric oxide that strike

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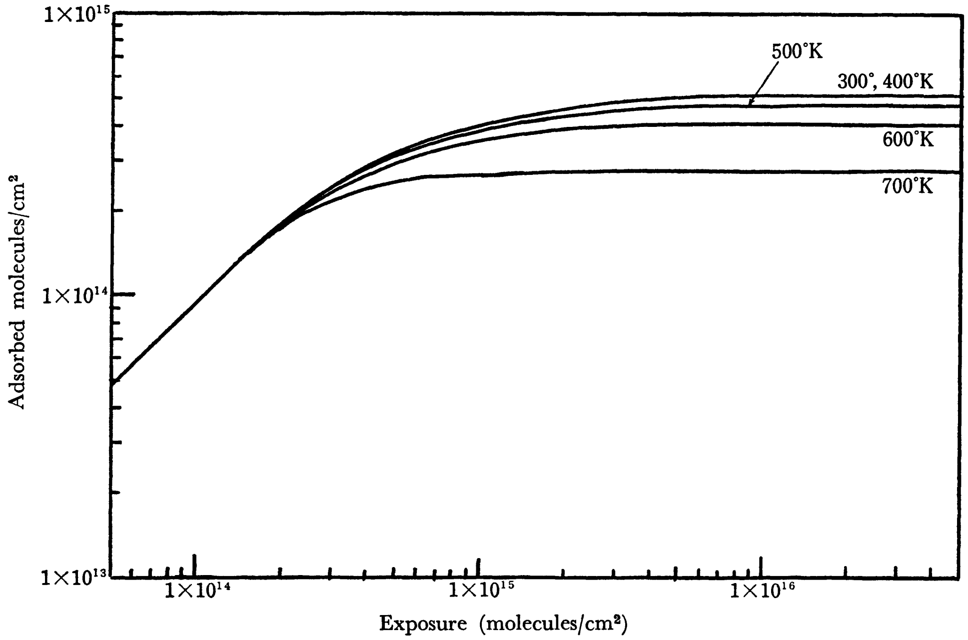

Fig. 2. Surface coverage as a function of exposure.

the filament during the adsorption process, $N_{(e)}$, is calculated from the recorder trace of the omegatron, while the number of molecules adsorbed, N, is obtained by rapid flashing into the closed system, as has been described above. The relation between the number of molecules colliding with the filament at various temperatures and those adsorbed is shown in Fig. 2. The saturation coverage (θ=1) of nitric oxide was 5.2×10^{14} molecules/cm² at 300°K, about one-third of that on tungsten (1.4×10^{15} molecules/cm²).[17] When the rhenium temperature was increased, the saturation coverage of nitric oxide decreased, as Fig. 2 shows. Assuming that the number of metal surface atoms is 1.5×10^{15} atoms/cm², these are equivalent to a Re: NO ratio of about 3:1 and to a W:NO ratio about 1:1. It seems that a considerable number of bare sites exist on rhenium, even for the full coverage of the nitric oxide adsorption.

From the curve in Fig. 2, the sticking probability, s, can be calculated by means of the following equation:

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

The dependence of the sticking probability on the coverage at various temperatures is shown in Fig. 3. The initial sticking probability is close to unity. Such a high value has not been seen for other gases.[20–22,25,26] Therefore, the Re-N_2 system was studied by the same method for the sake of comparison. The saturation coverage of nitrogen on rhenium was 1.08×10^{14} molecules/cm², this value agreed well with the previously-reported values, 1.5×10^{14} molecules/cm² at 291°K,[21] 7×10^{13} molecules/cm² at 300°K,[20] and 8.9×10^{13} molecules/cm² at 300°K.[26] The initial sticking probability was 0.003; this also agreed well with the previously-reported values of 0.0024[21] and 0.0022,[26] but it differed from that of 0.009.[20] This difference can be accounted for by differences in the polycrystalline wires used.

The results obtained by the usual method, using the flash desorption at a constant flow rate,[10] also agreed well with those of the present method.

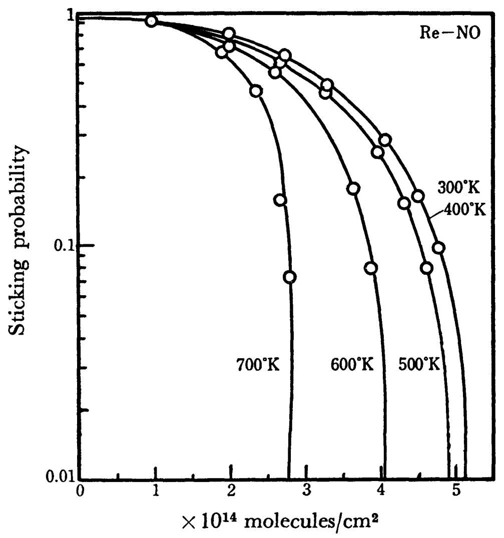

Fig. 3. Sticking probability as a function of surface coverage.

The saturation coverage of nitric oxide is 4.8 times as much as that of nitrogen on the same rhenium. This ratio agrees well with that on tungsten.[17] However, the saturation coverage on rhenium is smaller than that on tungsten.

The initial sticking probability of the nitric oxide adsorption is very high compared with the nitrogen adsorption on rhenium. We consider that one of the reasons for such a high value is probably that the electron in the nitric oxide molecule transfers easily to the vacant d-orbital in rhenium, because the ionization potential of nitric oxide (9.5 eV) is lower than that of nitrogen (~16 eV).[29]

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Rates of Adsorption and Desorption. At various combinations of the pressure of nitric oxide and the exposure time needed to obtain the same exposure, it was found that the amounts of adsorptions were always the same. These results show that the rate of adsorption depends on the first-power of the pressure. The rate of adsorption at a constant pressure and temperature may, then, be expressed as:

$$dN/dt = K\cdot P(1-\theta)^n,$$

where K and n are constants and where P is the nitric oxide pressure.

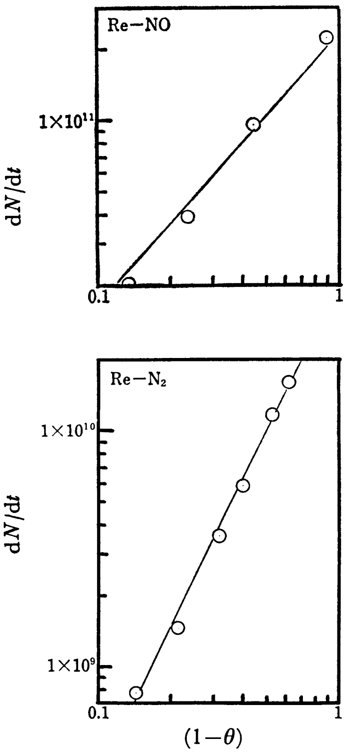

Fig. 4. The relation between the rate of adsorption and $(1-\theta)$.

For the nitric oxide and the nitrogen adsorption at a constant pressure and 300°K, the dependence of the rate of adsorption on the vacant site, $(1-\theta)$, is shown in Fig. 4. On the nitric oxide adsorption, it was found that the rate of adsorption was proportional to $(1-\theta)$ for surface coverages between 0.1 and 0.8. This indicates that the nitric oxide molecules are adsorbed non-dissociatively on rhenium. On the nitrogen adsorption, it is shown that the adsorbed nitrogen exists dissociatively, because the rate of adsorption was proportional to $(1-\theta)^2$.

When the adsorbed nitric oxide or nitrogen is desorbed at a definite temperature in the closed system, the rate of desorption may be simply written as:

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

where K' is a rate constant of the $K'=\nu\exp(-E/RT)$ form and where n' is the order of the desorption. In the Re-NO system, the nitric oxide is decomposed with a rise in the rhenium temperature and is desorbed as nitrogen. The relation between the rate of desorption and the surface coverage is shown in Fig. 5. As can be seen, the rate of the desorption of nitrogen from both nitric oxide and nitrogen layers is roughly proportional to θ^2. At such high temperatures, the re-adsorption can be neglected.

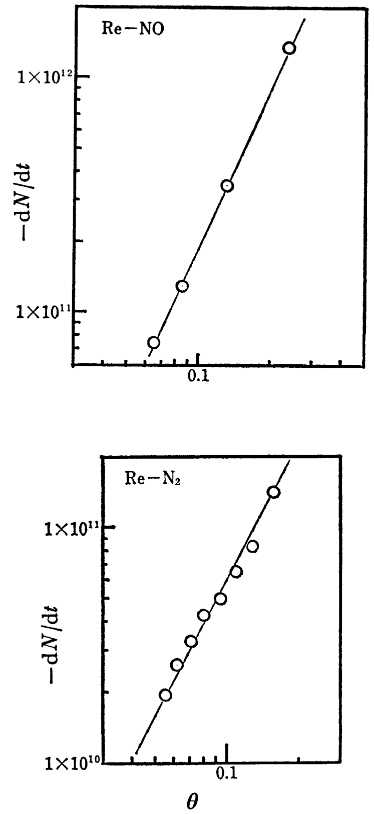

Fig. 5. The relation between the rate of nitrogen desorption and θ.

Desorption Spectra. *1) Desorption from a Nitric-oxide Monolayer on Rhenium*: For the saturation coverage of nitric oxide, the desorption spectra are shown in Fig. 6. The evolution of nitric oxide (mass 30) begins at about 350°K. The temperature of the desorption-peak maximum was about 450°K, and above 900°K no further desorption of nitric oxide was observed. The amount of nitric oxide desorbed corresponds to about 0.5% of the total amount of nitric oxide at saturation coverage.

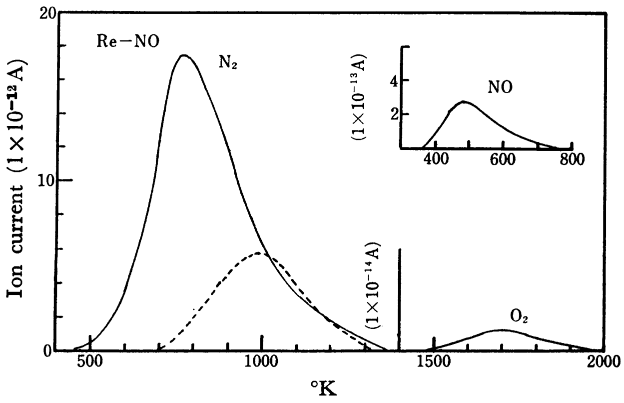

Fig. 6. The desorption spectra from a nitric oxide monolayer on rhenium.
Dashed curve denotes nitrogen from nitrogen monolayer.

For the desorption of nitrogen from a nitric oxide monolayer, the temperature at which the desorption rate was at its maximum, T_p, was 775°K, and the greater part of the nitrogen was desorbed before the temperature reached to 1300°K. The T_p of nitrogen desorption from a nitric oxide monolayer is lower than that from a nitrogen monolayer by about 200°K.

The oxygen desorption was seen at a considerably high temperature, and the T_p of oxygen was about 1700°K. The amount of oxygen desorbed was relatively small. From these results, it seems that the majority of the oxygen from nitric oxide evaporates as rhenium oxide.

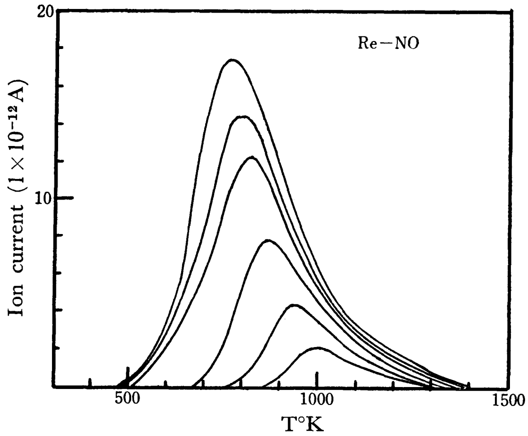

Fig. 7. The desorption spectra from various initial coverages of nitric oxide.

2) Desorption of Nitrogen from a Partial Coverage of Nitric Oxide on Rhenium: The nitrogen desorption spectra for various initial coverages of nitric oxide ($\theta\simeq0.1$—1.0) at 300°K are shown in Fig. 7. The T_p of the nitrogen desorption monotonously shifts to higher temperatures with a decrease in the coverage. On the chemisorption of nitric oxide on tungsten, a retrograde behavior of T_p above $\theta=0.8$ was observed in the nitrogen desorption spectra, and two ω mode peaks (ω_1, ω_2) were observed in the desorption spectrum.[17] However, no such behavior was observed for the nitric oxide adsorption on rhenium. Yates *et al.*[17] state that vacant sites are necessary for the decomposition of nitric oxide on tungsten. If this assumption is true, the fact that a retrograde T_p behavior was not found on rhenium at a high coverage can be understood from the fact that the vacant sites already existed on the rhenium surface, as has been mentioned above.

The desorption spectra from the very low coverages of nitric oxide on rhenium resemble those from the very low coverages of nitrogen. This behavior is reasonable, since the dissociation of nitric oxide at a very low coverage and at an elevated temperature would produce a dilute layer of adsorbed nitrogen and oxygen; the desorption of nitrogen should, under these conditions, be uninfluenced by the small oxygen coverage. Therefore, the processes of adsorption, dissociation, and desorption may be simply expressed as follows:

$$NO_{(g)} \longrightarrow NO_{(a)} \tag{1}$$

$$NO_{(a)} \longrightarrow N_{(a)} + O_{(a)} \tag{2}$$

$$2N_{(a)} \longrightarrow N_{2(g)} \tag{3}$$

Equations (2) and (3) show the reactions during the heating process. We consider that the rate of the process (2) is faster than that of the process (3), since the rate of nitrogen desorption is roughly proportional to θ^2.

3) Desorption of Nitrogen from a Nitrogen Layer on Rhenium: Although studies of the nitrogen adsorption of rhenium had previously been made,[20,21,26] the present experiments were carried out to compare it with the nitric oxide adsorption. An α state was not found in the nitrogen desorption spectra from the nitrogen layer. This result agreed with that of Yates *et al.*[26] Although the β state from nitrogen layer on tungsten was separated into two states, β_1 and β_2,[11,13,15,16] the β state from the nitrogen layer on rhenium was only one state (corresponding to β_2); this finding agreed with those of other papers.[20,21,26] Since the desorption energy of nitrogen on rhenium is lower than that on tungsten, the binding force with rhenium may be said to be weaker than that with tungsten.[26] Therefore, it seems that the β_1 (weaker than β_2) adsorption may not occur; the lack of a β_1 state may be a reason why many vacant sites remain on rhenium for the nitric oxide adsorption compared with those on tungsten.

Summary

1) The saturation coverage of nitric oxide on rhenium is 5.2×10^{14} molecules/cm^2, and the sticking probability is close to unity in the initial stage of adsorpion at room temperature.

2) Nitric oxide adsorbs nondissociatively on rhenium at room temperature. The rate of adsorption is proportional to $(1-\theta)$.

3) As the rhenium temperature is increased, the saturation coverage of nitric oxide decreases.

4) The evolution of nitric oxide (mass 30) begins at about 350°K, and the amount of nitric oxide corresponds to about 0.5% of the saturation coverage.

5) The rate of the desorption of nitrogen from a nitric oxide layer is proportional to θ^2.

6) The T_p of nitrogen desorption from a nitric oxide monolayer is lower than that from a nitrogen monolayer by about 200° as a result of the interactional effect in the adsorbed layer of oxygen.

7) A small fraction of the oxygen from the nitric oxide layer desorbs above 1500°K as molecules; it seems that the rest of the oxygen evaporates as rhenium oxide.

8) At a high coverage of nitric oxide, the retrograde behavior of T_p for nitrogen desorption is not observed.

9) At a very low nitric oxide coverage, the desorption spectra resemble those from a very low coverage of nitrogen.

10) The saturation coverage of nitrogen on rhenium is 1.08×10^{14} molecules/cm^2, and the initial sticking probability is 0.003 at room temperature.

11) Nitrogen adsorbs dissociatively at room temperature. The rate of adsorption is proportional to $(1-\theta)^2$.

12) For nitrogen adsorption at room temperature, an α state is not found, and the β state is only one state.

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