The Coadsorption of Nitric Oxide, Nitrogen, and Oxygen on Rhenium

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(Received March 8, 1971)

The coadsorption of nitric oxide, nitrogen, and oxygen on a polycrystalline rhenium filament was studied using flash desorption mass-spectroscopy. Substitutional desorption was not observed during the adsorption of nitric oxide, nitrogen, or oxygen on preadsorbed leayers. No oxygen or nitrogen adsorbs on rhenium saturated with nitric oxide. However, nitric oxide adsorbs on rhenium saturated with nitrogen or oxygen. The strength of the chemisorption bond between rhenium and adsorbed species becomes weaker in the order of: nitric oxide, oxygen, and nitrogen. When the same amount of nitric oxide molecules exist in various coadsorbed layers, the Tp of the nitrogen desorption spectrum from these layers is shifted to a lower temperature with an increase in the number of oxygen atoms in them, because the strength of the chemisorption bond of Re–N is weakened by the strongly-bonded Re–O. No desorption of the nitric oxide molecule from a coadsorbed layer of the "N_2+O_2" on rhenium was observed.

In the investigation of chemical reactions between metal and gas, studies of the chemisorption which precede these reactions will lead to a general understanding of the mechanism of chemical reactions. There has been much work done on the chemisorption of common gases, such as nitrogen,[1–6] oxygen,[7–11] hydrogen,[12,13] and carbon monoxide,[14–17] on metal surfaces.

The investigation of the chemisorption of nitric oxide, which possesses an odd number of electrons, is of interest. In a previous paper,[18] a study of the chemisorption of nitric oxide alone on rhenium has been reported.

In general, the temperature which gives the maximum rate of the desorption, Tp, and the peak height in the desorption spectrum from chemisorbed layers may be related to the desorption energy of the adsorbed species, so that different desorption spectra may be displayed by various adsorbed species with different surface coverages. Moreover, desorption spectra may be also changed by being affected by the coexistence of different adsorbed species. Thus, although the investigation of the coadsorption on metal surfaces is of interest, there have been only a few studies in this field.[8,19–22]

In the present investigation, the coadsorption of nitric oxide, nitrogen, and oxygen and the replacement of chemisorbed gases on a polycrystalline rhenium filament have been studied using flash desorption mass-spectroscopy.

Apparatus

The bakeable, ultra-high-vacuum apparatus used in this study was similar to that used in a previous work[18] except that it had two gas-supply system. It is shown in Fig. 1 schematically. The reaction systems, the volume of which was 0.8 *l*, contained a polycrystalline 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 ultimate pressure, read with a Bayard-Alpart gauge (B-A gauge), was 3×10^{-10} Torr in the system after a rigorous outgassing. 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 also used as a partial-pressure gauge; it had a sensitivity of 12 Torr^{-1} for N_2, 11.8 Torr^{-1} for NO, and 11 Torr^{-1} for O_2. The B-A gauge was used only in the ultimate-pressure measurement because the nitric oxide is dissociated by a hot filament of the gauge. The rhenium filament was heated to 2200°K using a transistor control circuit, as has been described previously.[18] The filament temperature was determined from a resistance-temperature relationship for rhenium;[23] above 1000°K, its temperature was measured with a micro optical pyro-

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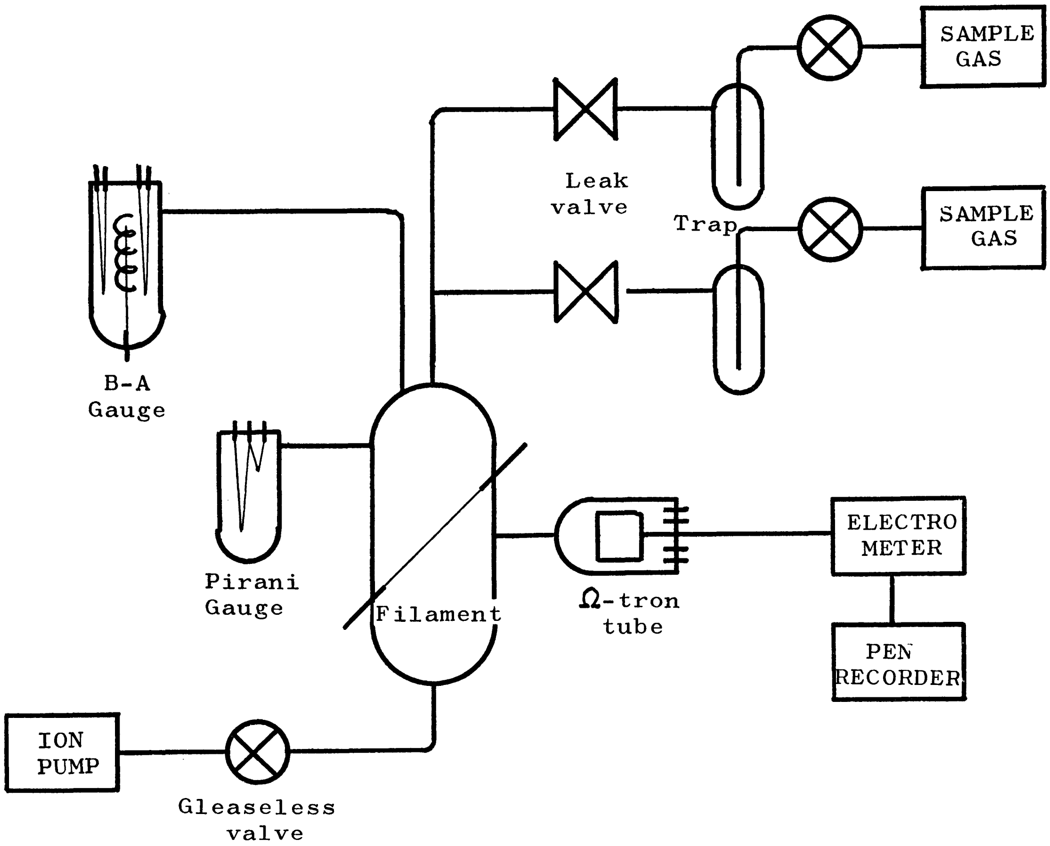

Fig. 1. Schematic drawing of Ultrahigh-vacuum apparatus for flash desorption mass spectroscopy.

meter.

The nitric oxide and nitrogen were prepared by the methods described in the previous paper. The oxygen was prepared by the thermal decomposition of high-purity potassium permanganate. The gas evolved was purified by liquid-nitrogen trap-to-trap distillation. No impurities up to mass 200 of any of the sample gases were detected by means of the omegatron mass spectrometer.

Procedure

Amount of Adsorption. The rhenium filament was purified by heating it at about 2000°K in oxygen of 1×10^{-6} Torr for several hours. The rhenium filament was then flashed to clean at 2200°K in a vacuum prior to the adsorption experiments, and then allowed to cool at room temperature. After nitric oxide had been passed through to obtain the saturation coverage, the system was evacuated; nitrogen or oxygen was then passed through to allow it to adsorb sufficiently. Such coadsorbed layers are expressed as "$NO+N_2$" or "$NO+O_2$". After the system had then been evacuated until the pressure dropped to 5×10^{-9} Torr, the rhenium filament was flashed at 2200°K in a closed system. The amount of molecules desorbed can be calculated from the pressure and the volume of the system. In the nitric-oxide adsorption, the number of molecules adsorbed is twice the number of molecules desorbed, because the desorbed gas is nitrogen.

Desorption Spectra. After the coadsorbed layer was formed, as has been described above, the slow flash desorption runs were initiated by using a transistor control circuit while the system was being evacuated. Ion currents of the omegatron mass spectrometer for each mass were recorded on the chart recorder.

Substitutional Desorption. For example, on the coadsorption of "$NO+O_2$", the ion current of the omegatron mass spectrometer corresponding to nitric oxide (preadsorbate) was measured during the adsorption of oxygen on rhenium saturated with nitric oxide. The substitutional desorption of nitric oxide could be detected from the change in this ion current

Results and Discussion

The amounts of nitrogen desorbed from various coadsorbed layers are shown in Table 1. The desorption spectra of nitrogen from the coadsorbed layers are shown in Fig. 2, while the temperatures of the desorption-peak maximum, *T*p, are also shown in the second column of the table.

"*$NO+N_2$*". The substitutional desorption of nitric oxide was not observed during the adsorption of nitrogen on rhenium saturated with nitric oxide. Both the amount of nitrogen desorbed and the desorption spectrum of nitrogen from the "$NO+N_2$" layer were the same as those from a nitric oxide monolayer on rhenium. Therefore, nitrogen does not adsorb on the saturated nitric oxide layer on rhenium.

"*$NO+O_2$*". The substitutional desorption of nitric oxide was not observed in this case. Both the amount of nitrogen desorbed and the desorption spectrum of nitrogen from the "$NO+O_2$" layer were

TABLE 1. THE AMOUNT OF NITROGEN DESORBED AND THE Tp IN THE NITROGEN DESORPTION SPECTRUM FROM VARIOUS ADSORBED LAYERS ON RHENIUM

Layer	N_2 (desorbed) (molecules/cm^2)	Tp (°K)
NO	2.6×10^{14}	775
$NO+N_2$	2.6×10^{14}	775
$NO+O_2$	2.6×10^{14}	775
N_2+NO	3.4×10^{14}	775
O_2+NO	3.4×10^{13}	850
N_2	1.08×10^{14}	970
N_2+O_2	1.08×10^{14}	820
O_2+N_2	—	—

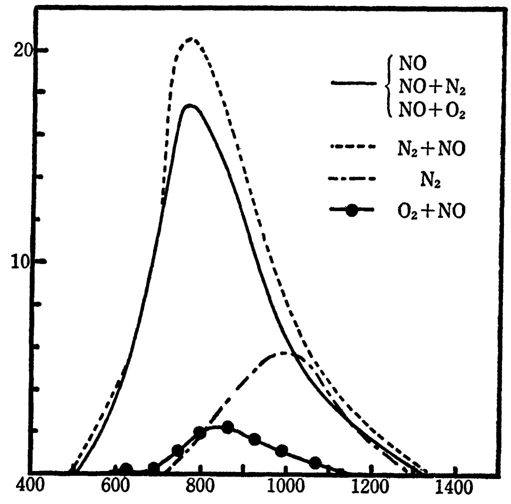

Fig. 2. Nitrogen desorption spectra from various coadsorbed layers on rhenium.

the same as those from a nitric oxide monolayer on rhenium. Although the oxygen desorption was observed at temperatures above 1500°K,[18] the majority of the oxygen evaporates as rhenium oxide at such a high temperature. Therefore, the detection of the amount of oxygen adsorbed is very difficult from the pressure burst in the flash-desorption experiment. Thus, it is impossible to know whether or not oxygen adsorbs on rhenium saturated with nitric oxide. If oxygen adsorbs on this surface, there may be some influence on the desorption spectrum of nitrogen. However, even the exposure of oxygen was changed in the coadsorption of "$NO+O_2$", the desorption spectrum of nitrogen from this layer being the same as that from a nitric oxide monolayer. From this fact, it may be considered that oxygen is not adsorbed on rhenium saturated with nitric oxide.

"N_2+NO". No substitutional desorption of nitrogen was detected during the adsorption of nitric oxide on the preadsorbed nitrogen layer. The Tp of the desorption spectrum of nitrogen from the "N_2+NO" layer was the same as that from a nitric-oxide monolayer, but the amount of nitrogen desorbed from this coadsorbed layer was 3.4×10^{14} molecules/cm^2, while the nitrogen desorbed from a nitric-oxide monolayer was 2.6×10^{14} molecules/cm^2. If the nitric-oxide molecule can be adsorbed on a site other than that occupied by preadsorbed nitrogen atoms, the nitric oxide of 3.04×10^{14} molecules/cm^2 will be adsorbed on rhenium saturated with nitrogen, as is shown in Fig. 3. (Nitrogen adsorbs dissociatively on rhenium.) From the amount of nitrogen desorbed, it is evident that an excess of 1.6×10^{14} molecules/cm^2 of nitrie oxide was adsorbed. The desorption spectra of nitric oxide from a nitric oxide monolayer and the "N_2+NO" layer on rhenium are shown in Fig. 4. The amount of desorbed nitric oxide as a molecule from the "N_2+NO" layer is more than that from a nitric-oxide monolayer. Furthermore, as is evident from Fig. 2, at an early stage the rate of nitrogen desorption from the "N_2+NO" layer in the nitrogen desorption spectrum is faster than that from a nitric-oxide monolayer. When nitric oxide was adsorbed on a preadsorbed nitrogen layer with a half coverage, "$N_2(1/2)+NO$", the amount of nitrogen desorbed from this layer was 3.0×10^{14} molecules/cm^2. By calculations similar to those in the case of "N_2(full)$+NO$", it can be concluded that an excess of 8×10^{13} molecules/cm^2 of nitric oxide is adsorbed. This is half the value of that from the "N_2(full)$+NO$" layer. The amount of the excess nitric oxide is proportional to the amount of preadsorbed nitrogen. From these facts, we can consider that some nitric oxide molecules were induced by the preadsorbed nitrogen atoms and were weakly held on it.

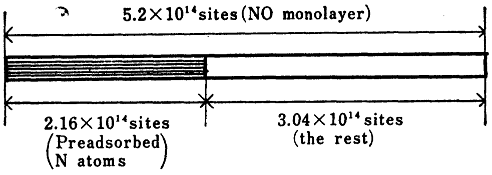

Fig. 3. The number of vacant and adsorbed sites in the nitrogen monolayer.

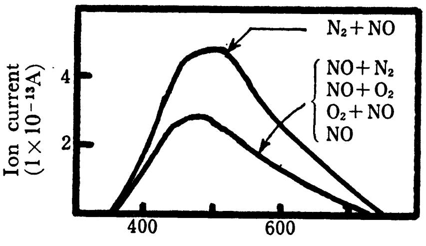

Fig. 4. Nitric oxide desorption spectra from various coadsorbed layers on rhenium.

"O_2+NO". No substitutional desorption of oxygen during the adsorption of nitric oxide was observed. Since the amount of nitrogen from the "O_2+NO" layer was 3.4×10^{13} molecules/cm^2, it shows that nitric oxide can adsorb on rhenium saturated with oxygen. The Tp of nitrogen desorption from this coadsorbed layer is 850°K.

This fact may suggest that the number of adsorptive sites for oxygen atoms is less than that for nitric oxide molecules. (Oxygen adsorbs dissociatively,[10] and nitric oxide adsorbs nondissociatively,[18] on rhenium.) If this is so, in the slow-flash desorption experiment of nitric-oxide adsorption, the desorption of oxygen from the decomposition of nitric oxide must be observed in the temperature region of the nitrogen desorption. However, the desorption of neither molecular nor atomic oxygen was detected in this temperature region in these experiments.

If the oxygen atoms adsorbed are immobile, they will occupy two sites for oxygen adsorption, and some adsorptive sites will remain on the rhenium surface as vacant sites.[24] It is possible that nitric oxide adsorbs on these vacant sites. Oxygen adsorption was made on the rhenium surface while heating the rhenium filament to a high temperature at which adsorbed oxygen atoms were able to migrate over the surface;[25] the filament was afterward allowed to cool to room temperature. When this surface was exposed to nitric oxide, the amount of nitric oxide adsorbed on it was found to be about a half of that on the surface saturated with oxygen at room temperature. From the fact that, in the nitric-oxide adsorption, the desorption of neither molecular nor atomic oxygen is observed in the temperature region of nitrogen desorption, as has been mentioned above, nitric oxide can be said probably to adsorb on vacant sites formed with oxygen adsorption at room temperature, because the nitric oxide adsorbs nondissociatively.

On the other hand, although the desorption of nitric oxide molecules from the "O_2+NO" layer was observed by a slow-flash desorption experiment (Fig. 4), the nitric oxide desorption from a partial coverage of nitric oxide which desorbs the same amount of nitrogen as that from the "O_2+NO" layer was not observed. Moreover, the oxygen desorption from the "O_2+NO" layer was observed in the temperature region of the nitrogen desorption. We consider that some oxygen from the decomposition of nitric oxide in the "O_2+NO" layer was desorbed in this temperature region, for all the available sites for adsorption in first layer were occupied by oxygen atoms and nitric oxide molecules. It seems that a weakly-held adsorption of nitric oxide, such as could be seen in the coadsorption of the "N_2+NO", is also present in the "O_2+NO" layer. As has been mentioned above, it is considered that the nitric oxide adsorption in the "O_2+NO" layer has two types of binding states, that is, a gap-filling state and a weakly-bonded state on the immobile preadsorbed oxygen layer at room temperature. Although the *T*p of nitrogen desorption from the "O_2+NO" layer was 850°K, the *T*p of that from the partial coverage of nitric oxide which gave the same amount of nitrogen desorbed as that from the "O_2+NO" layer (the same amount of nitric oxide adsorbed) was 1000°K. There are more oxygen atoms in the "O_2+NO" layer than in the partial coverage of nitric oxide (the same amount of nitric oxide). This behavior may be interpreted as follows——the bonding strength of Re–N may be weakened by the oxygen adsorption, which binds strongly with rhenium in adjacent sites. We may thus consider that the nitrogen on the surface desorbs more easily and that the *T*p of nitrogen desorption is shifted to a lower temperature (from 1000°K to 850°K).

"N_2+O_2". No substitutional desorption of nitrogen was also observed in this case, either. No desorption of nitric oxide molecule was observed from this layer during the slow-flash experiment. The amount of nitrogen desorbed from the "N_2+O_2" layer was the same as that from a nitrogen monolayer, but its *T*p was 820°K and it was considerably shifted to a lower temperature. It is considered that the bonding strength of Re–N was also weakened as a result of the adsorption of oxygen atoms between the adsorbed nitrogen atoms, as has been described above. The *T*p of nitrogen desorption from this coadsorbed layer is lower than that (870°K) from the partial coverage of nitric oxide giving the same amount of desorbed nitrogen. It is believed that the *T*p might be shifted to a lower temperature, because there are more oxygen atoms in the "N_2+O_2" layer than in the partial coverage of nitric oxide (with the same amount of nitrogen atoms). Furthermore, the *T*p of nitrogen desorption from the "N_2+O_2" layer is lower than that from the "O_2+NO" layer. It seems that the probability for the recombination of adsorbed nitrogen atoms is high, because the number of nitrogen atoms in the "N_2+O_2" layer is more than that in the "O_2+NO" layer.

"O_2+N_2". No desorption of either nitrogen or nitric oxide was observed by the slow-flash experiment. Therefore, nitrogen is not adsorbed on rhenium saturated with oxygen.

Conclusion

Since both the desorption spectra and the amounts of nitrogen desorbed from the "NO+N_2" and the "NO+O_2" layers were the same as those from the nitric oxide monolayer, it is considered that neither nitrogen nor oxygen is adsorbed on rhenium saturated with nitric oxide. Nitric oxide, however, adsorbs not only on vacant sites in the first layer, but on sites in the second layer on rhenium saturated with nitrogen or oxygen. Therefore, the bonding strength between rhenium and adsorbed species becomes weaker in the order of: nitric oxide, oxygen, and nitrogen.

When the more oxygen atoms exist in coadsorbed layers which include the same amount of nitrogen atoms, the *T*p of the nitrogen desorption is shifted to a lower temperature.

No nitric oxide was detected in the desorption from a mixed nitrogen-oxygen layer. This indicates that nitric oxide was not produced in the adsorption and the desorption processes. Further, nitrogen does not adsorb on an oxygen-saturated rhenium surface, because the adsorption site for nitrogen is occupied by the oxygen atoms.

The author wishes to express his deep thanks to Professor Takuya Hamamura of this Institute, to Professor Kumasaburo Kodera and Dr. Masaru Onchi of Kyoto University for their kind discussions and encouragement, and to Dr. Minoru Ozasa of the Matsushita Electronics Corporation, who made the spectroscopic analysis of rhenium.

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