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DECOMPOSITION OF NO₂ TO NO AND O ON Pt(111)

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We have studied the adsorption and subsequent chemistry of NO₂ on Pt(111). At low temperatures (~120 K), NO₂ adsorbs molecularly on this platinum surface. The decomposition of NO₂ to NO and O becomes appreciable at temperatures above 240 K. The decomposition of NO₂ on Pt(111) provides a very efficient source of adsorbed O on this surface. The coverage of adsorbed O from the source can be significantly larger than the saturation coverage obtained from adsorption of O₂.

The importance of the chemistry of oxides of nitrogen on Pt to the automobile exhaust catalyst has stimulated a significant amount of fundamental work on these systems. However, to date there is little literature to be found on the chemistry of NO_2 on well characterized Pt surfaces. In this letter we present the initial results of our studies of the decomposition of NO_2 on Pt(111).

We have carried out LEED and temperature programmed desorption (TPD) experiments on NO_2 as well as coadsorbed NO_2 and O_2 .

The experimental setup has been described elsewhere [1]. It is difficult to handle NO_2 in a conventional stainless steel gas handling line without significant amounts of decomposition. We found that the use of a copper gas handling line which had been heavily oxidized by previous exposure to NO_2 allowed us to obtain high purity exposures of NO_2 to the platinum sample.

Exposure of 3 L of NO₂ to a Pt(111) surface at 120 K results in a disordered overlayer which leads to an increased background of the LEED pattern for the clean Pt(111) surface. This overlayer is slightly electron beam sensitive. Exposure of the overlayer to the LEED electron beam for several minutes starts to produce a (2×2) structure on the sample area under the electron beam. Therefore, care was taken to minimize the exposure of the overlayer to the electron beam. Upon warming of the crystal to 240 K a very diffuse (2×2) overlayer structure begins to form. The (2×2) structure is quite sharp at 285 K. Both O₂ and NO are known to form (2×2) overlayers on Pt(111).

Fig. 1 shows the results of temperature programmed desorption experiments



Fig. 1. Thermal desorption spectra generated following exposures of 3 and 60 L of NO_2 at 120 K. A linear temperature ramp of 7 K/s was used.

for NO₂ adsorbed on Pt(111) at 120 K. The only thermal desorption species are NO and O_2 . The NO desorbs as a single peak at 325 K, with a small high temperature shoulder.

Adsorption of NO followed by desorption results in a peak in the NO desorption at the same temperature, again with a small high temperature shoulder. This shoulder has been ascribed to binding of NO at defect sites [3]. We observe no O_2 or N_2 from adsorption of NO on this surface. At low exposures the O_2 desorption is the same as is obtained from exposing the surface to O_2 . However, at higher exposures there are two distinct differences between the O_2 desorption from NO₂ exposure and from O_2 exposure. First, the amount of O_2 desorbed following NO₂ exposure can be significantly larger than the amount obtained from a saturation oxygen (2 × 2) overlayer. In addition, at high exposures of NO₂ a low temperature shoulder appears in the O_2 desorption. The onset of desorption for this low temperature shoulder shoulder develops as low as 420 K. Auger spectra taken after the TPD experiment showed no remaining nitrogen or oxygen.

We have also carried out experiments in which we have coadsorbed O_2 and NO_2 on this surface. These experiments were carried out with natural isotopic abundance O_2 and isotopically pure ${}^{18}O_2$. In these experiments the saturated oxygen (2 × 2) overlayer was produced followed by adsorption of NO_2 at 120 K. Fig. 2 shows the TPD results from the ${}^{18}O_2/NO_2$ coadsorption experiment. There are three important points to be recognized in the coadsorption results: (1) The additional oxygen from the NO_2 is observed in both the low temperature shoulder and the O_2 peak at 450 K. (2) The oxygen is isotopically mixed among the O_2 desorption peaks. ${}^{18}O^{18}O_1$ and ${}^{16}O^{16}O$ are all seen throughout the oxygen desorption temperature range. In particular the preadsorbed ${}^{18}O$ contributes to the low temperature shoulder of the O_2



Fig. 2. Thermal desorption spectra generated from the coadsorption of ${}^{18}O_2$ and NO_2 . A linear temperature ramp of 7 K/s was used.

desorption. (3) A small amount of N¹⁸O is observed (the N¹⁸O is down by an order of magnitude from the N¹⁶O). The N¹⁸O desorption peak is identical in peak temperature and shape to the N¹⁶O desorption peak at 325 K. Small amounts of exchange between ¹⁸O and N¹⁶O on Pt(111) has been observed previously by Gland and Sexton [2].

We observe NO₂ to decompose to NO + O on Pt(111). We observe only one peak in the NO desorption following NO₂ adsorption even at high coverages. Previous work had shown that an additional NO desorption peak occurs at 200 K for high coverages of NO on Pt(111), and that this persists when NO is coadsorbed with O₂ [2,3]. We do not observe NO in this temperature range. This indicates that the decomposition of NO₂ is not appreciable below this temperature.

Decomposition of small amounts of the NO₂ at low temperature cannot be ruled out by the absence of the low temperature NO desorption since this is a higher coverage state of NO. However, our experiments are in a coverage range such that if a major fraction of the NO₂ were dissociatively adsorbed the 200 K NO desorption would be observed. We estimate that less than 10% of the NO₂ decomposes on adsorption at 120 K in our high coverage experiments. This is also consistent with our LEED results where we see the formation of a (2×2) structure only above 240 K. The NO desorption peak at 325 K in fig. 1 has an onset at ~ 245 K. This peak has the same peak temperature and shape as we observe following NO adsorption. Thus it is not likely that the desorption is reaction limited at any temperature above 245 K. The onset of observation of the (2×2) ordering at 240 K must then be indicative of the onset of appreciable decomposition of NO₂. The decomposition of NO₂ provides an efficient source for high coverages of oxygen on the surface. The isotopic coadsorption experiment indicates that this oxygen is not divided into two well defined states (the (2×2) and high coverage state). A likely explanation for the low temperature shoulder in the oxygen desorption is a desorption activation energy which is coverage dependent because of strong lateral interactions at high coverage. A model which would have a well defined binding site for the initial oxygen filling the (2×2) structure and a separate binding site for the high coverage oxygen with no mixing is ruled out by the isotopic mixing we observe in the NO₂/¹⁸O₂ coadsorption experiment.

The NO₂ decomposition we observe brings up the possibility that oxygen exchange with NO may occur via an NO₂ intermediate without the necessity for dissociative adsorption of NO. That is, process (1) may account for the N¹⁸O we observe in the NO₂/¹⁸O₂ coadsorption.

$$N^{16}O + {}^{18}O \rightarrow [{}^{18}ON^{16}O] \rightarrow N^{18}O + {}^{16}O.$$
 (1)

Certainly the possibility of equilibrium between NO_2 and NO + O exists in the temperature range near 240 K.

These initial experiments on the decomposition of NO₂ on Pt(111) indicate: (1) that the decomposition becomes appreciable at ~ 240 K, (2) that high coverages of oxygen may be obtained on Pt(111) by the decomposition of NO₂ and that at these high coverages the Pt-O interaction is weakened. In addition the decomposition of NO₂ to NO + O indicates the possibility that isotopic exchange of oxygen with coadsorbed NO may occur via an NO₂ intermediate in the absense of dissociative adsorption of NO. Further coadsorption experiments of NO with ¹⁸O₂ are planned to test this possibility.

The formation of higher coverages of oxygen on Pt, which is presumably less tightly bonded, indicates that NO_2 may act very differently as an oxidant than O_2 in catalytic oxidation over Pt.

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References

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