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In Situ Characterization of the Surface Reaction between Chemisorbed Ammonia and Oxygen on Pt{100}

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As the first step in the industrial synthesis of nitric acid, ammonia is oxidized over platinum to form NO.[1,2] This reaction, known as the Ostwald reaction, is biphasic, N_2 being the major product at surface temperatures below 600 K, whereas NO is formed at higher temperatures. At the high temperatures used industrially the platinum catalyst is lost at a fairly steady rate as PtO_2(g), which necessitates its regular replacement. Temperature-programmed reflection−absorption infrared spectroscopy, with simultaneous gas product analysis, has been employed here to provide the first in situ characterization of the surface reaction on Pt between preadsorbed O and NH_3, at temperatures between 150 and 600 K. The results demonstrate that the reaction selectivity between NO and N_2 is determined by the O adatom coverage.

The reaction was studied over polycrystalline Pt wire by Ya et al.[3] using secondary ion mass spectrometry. They found no evidence for surface intermediates and proposed a simple bimolecular reaction step to form NO; the formation of N_2 was attributed to the reaction between adsorbed NO and NH_3. The reaction was subsequently studied over polycrystalline wires[4−6] and Pt single-crystal surfaces,[7,8] with no alteration to the conclusions of Ya et al.[3] However, recent work on the reaction over Pt{111} and polycrystalline Pt[9−11] has led to a consideration of an $N + O \rightarrow NO$ recombination and the $NH + O \rightarrow NO + H$ exchange reactions, with gaseous N_2 being formed by N atom recombination.

Recently Bradley, Hopkinson and King,[12] hereafter BHK, performed an exhaustive molecular beam study of the reaction and deduced a new mechanism invoking O adatom coverage as the critical factor in determining if NO or N_2 is the major gaseous product. The following are the major ingredients of the BHK model, after initial stripping of adsorbed NH_3 to NH(a) by oxygen:

$$\mathrm{NH(a)} + 2\mathrm{O(a)} \rightarrow \mathrm{NO(a)} + \mathrm{OH(a)} \tag{1}$$

$$\mathrm{NO(a)} \rightarrow \mathrm{NO(g)}, \quad \theta_{\mathrm{O}} > 0.2\ \mathrm{ML} \tag{2}$$

$$\mathrm{NO(a)} \rightarrow \mathrm{N(a)} + \mathrm{O(a)}, \quad \theta_{\mathrm{O}} < 0.2\ \mathrm{ML} \tag{3}$$

$$2\mathrm{N(a)} \rightarrow \mathrm{N_2(g)} \tag{4}$$

Step 1 is dominant at relatively high O coverages (θ_O). Step 2 is favored if the oxygen adatom coverage is maintained above a critical coverage $\theta_C = 0.2$ monolayers (ML), while steps 3 and 4 dominate at low oxygen coverage. Thus, product selectivity in this model is determined by the steady-state oxygen adatom coverage on the surface. BHK also concluded that step 3 is thermodynamically, not kinetically, prohibited at higher oxygen coverages due to the low heat of NO dissociative adsorption at high oxygen coverages.[13,14] In the present work we provide a critical test of the BHK model by monitoring the generation and consumption of chemisorbed molecular species formed during the reaction by reflection−absorption infrared spectroscopy (RAIRS) and by correlating this with the gaseous products.

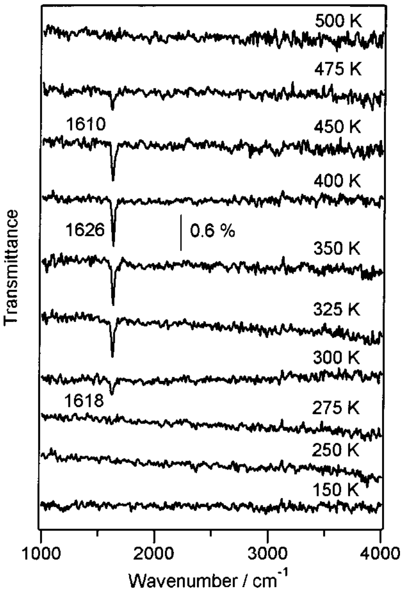

Figure 1. TP-RAIR spectra for the adsorption of 0.63 ML oxygen on Pt{100} at 300 K followed by 0.5 ML NH_3 at 150 K. The spectra were obtained at a heating rate of 1 K s^{-1}.

The experiments were conducted in a uhv chamber with a base pressure of 2×10^{-10} mbar and interfaced via KBr windows to a Mattson RS-2 FTIR spectrometer.[15] The crystal preparation, including the formation of the stable hex and the metastable (1 × 1) Pt{100} surfaces, has been described elsewhere.[16] Sharp LEED patterns were obtained with low background intensity. A time-resolved data acquisition program was employed to obtain temperature-programmed RAIR spectra at a heating rate of 1 K s^{-1} and a temperature resolution of 2 K $spectrum^{-1}$.

To follow the surface reaction between adsorbed NH_3 and O adatoms, oxygen was preadsorbed on the Pt{100} (1 × 1) surface at 300 K (to ensure dissociation to O adatoms) to coverages between 0.13 and 0.63 ML, and the surface was cooled to 150 K and dosed with 0.5 ML ammonia. These coverages were determined by reference to earlier sticking probability measurements.[17,18] The surface was then heated at 1 K s^{-1} to obtain TP-RAIR and TPD spectra.

The infrared results obtained with 0.63 ML O predosed are shown in Figure 1. A single infrared band at 1618 cm^{-1} grows into the spectra at 280 to 330 K, and is subsequently attenuated between 420 and 500 K. The band is readily assigned to the N−O stretch of adsorbed NO. In an independent experiment NO was adsorbed on the surface, and a band observed at 1599 to 1645

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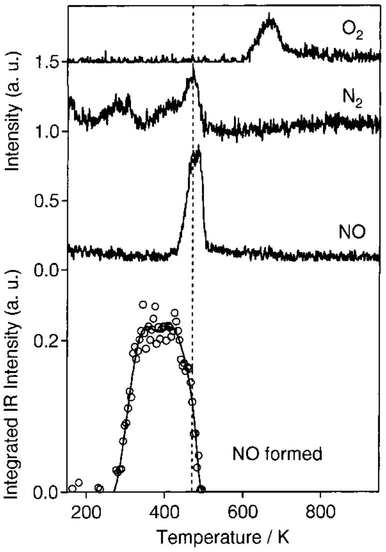

Figure 2. TPD spectra for O_2, N_2 and NO from the adsorption of 0.63 ML oxygen on Pt{100} at 300 K followed by 0.5 ML NH_3 at 150 K. The integrated intensity of the NO band in the corresponding TP-RAIR spectra is also shown. The data were obtained at a heating rate of 1 K s^{-1}.

cm^{-1}, dependent on coverage. By comparison of integrated intensities we estimate the maximum surface coverage of NO in the present experiment to be 0.32 ML. Two-thirds of the ammonia adsorbed has been converted to adsorbed NO.

In Figure 2 we show the TPD spectra for NO, N_2 and O_2, together with the TP-RAIRS data now presented as integrated NO band intensity vs temperature. The attenuation of the infrared signal from adsorbed NO is correlated with the TPD peaks for NO and N_2 at ~470 K. We therefore reach two important conclusions from this comparison.

(i) Adsorbed NO formed in the surface reaction at 300 K partly desorbs as gaseous NO and partly dissociates at ~470 K, the N adatoms rapidly associating to form gaseous N_2.

(ii) Since the NO coverage is stable between 330 and 430 K, the N_2 TPD at 380 K is not derived from the surface NO formed. Similarly the N_2 peak at 280 K, which appears before the appearance of NO(a), has an alternative origin. We assign these peaks to recombinative N_2 formation resulting from the complete stripping of NH_3(a) to N(a).

It now follows that, since N(a) recombinative desorption to N_2 begins at ~210 K, well below the temperature at which NO rapidly forms (~310 K, Figure 1), the surface reaction to NO(a) proceeds via incompletely stripped NH(a), as in the BHK model, step 1. This reaction may be more properly considered as a two-step process:

$$\mathrm{NH(a) + O(a) \rightarrow HNO(a)} \qquad (1a)$$

$$\mathrm{HNO(a) + O(a) \rightarrow NO(a) + OH(a)} \qquad (1b)$$

Since the HNO(a) intermediate has not been observed, either in this or the earlier studies, we conclude that it is a very short-lived intermediate; reaction 1a is rate-determining.

The activation energy for the surface reaction to form NO(a), step 1, was estimated in a series of isothermal experiments between 270 and 300 K using time-resolved RAIRS to determine the rate of NO(a) formation. This yields an activation barrier of 73 ± 4 kJ mol^{-1}, which is considerably smaller than the activation energy determined for the dissociation of NO adsorbed on Pt{100} and on polycrystalline Pt, of 120 kJ mol^{-1}.[19,20] The surface reaction to form adsorbed NO occurs at a significantly lower temperature than that for NO dissociation.

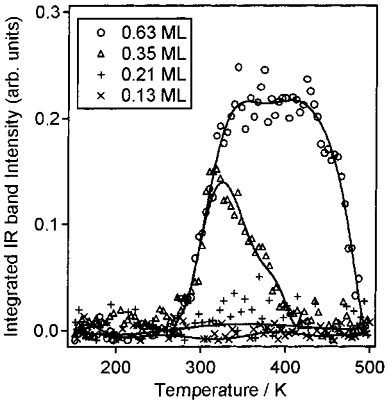

Figure 3. Integrated intensity of the NO band observed in TP-RAIRS following the adsorption at 150 K of 0.5 ML NH_3 on Pt{100} with oxygen precoverages of 0.63, 0.35, 0.21 and 0.13 ML.

For lower oxygen precoverages the TP-RAIRS and TPD data were quite different from the above. In Figure 3 we show samples of the TP-RAIRS data in the form of integrated N−O band intensity vs temperature plots. With oxygen precoverages of 0.21 ML and less, no surface NO could be detected. The preadsorbed oxygen is presumably consumed in stripping H atoms from NH_3, and the only N-containing species observed in simultaneous TPD spectra is N_2. At intermediate precoverages of oxygen, for example 0.35 ML, surface NO is again formed at ~300 K, but the band is now attenuated at temperatures above 310 K. This is the NO(a) dissociation reaction characterized by Fink et al.[19] and Pirug and Bonzel.[20] Again, in this coverage range no NO is observed in the gas phase: the NO formed in the surface reaction is quantitatively predissociated, the N adatoms combining to form gaseous N_2. These results therefore provide direct confirmation of steps 2, 3 and 4 in the BHK model. When the O adatom coverage is high, the overall reaction proceeds to gaseous NO, but when the O coverage is low, NO formed in the surface reaction dissociates, leading to gaseous N_2.

We note here that at the lowest O precoverage employed, 0.13 ML, a new infrared band was observed in TP-RAIRS. This band, at 1440 cm^{-1}, first appears at ~220 K, is fully developed at 275 K, and is attenuated between 340 and 370 K. The attenuation is accompanied by N_2 desorption. The band is assigned to adsorbed NH_2, based on the observation of the scissor mode for NH_2 on Pt{100} at 1450 cm^{-1} in an HREELS study.[21]

We have demonstrated that the selectivity of the overall reaction between ammonia and oxygen to NO or to N_2 on Pt{100} is controlled by the amount of oxygen adsorbed on the surface, in support of the BHK mechanism. At very low oxygen coverages adsorbed ammonia is stripped to NH_2(a) which decomposes at ~350 K to form gaseous N_2. At intermediate coverages adsorbed NO is formed in a surface reaction between NH and O, but the NO formed dissociates at a lower temperature (~350 K) than that characteristic of NO desorption (~475 K), and the product is again gaseous N_2. Above a critical steady-state coverage of oxygen, determined by BHK as 0.2 ML, NO dissociation is inhibited, and gaseous NO is therefore the main product of the reaction, at temperatures above ~470 K. Under steady-state conditions, the selectivity of the reaction can therefore be controlled by varying the oxygen coverage. As concluded by BHK,[12] high yields of NO *can* be obtained at low catalyst temperatures if the O_2/NH_3 mix is kept O_2 rich.

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