

Oxidation of Ammonia on Platinum

We have investigated the mechanism of ammonia oxidation on platinum using a molecular beam to sample in collision-free conditions the species from the surface for mass-spectroscopic analysis. With controlled molecular flow of the reactants to the surface, it was possible to achieve a molecular flux at the surface equivalent to immersion in a gas at pressures up to 10^{-2} mm Hg, while ensuring that reaction products had a negligible chance of returning to the surface. The technique was outlined in a previous communication¹. Preliminary results reported there supported the earlier conclusion of Fogel *et al.*² that oxidation proceeded directly to nitric oxide on the catalyst surface.

Detailed study of the effects of temperature and reactant fluxes to the surface has shown that the oxidation proceeds by a second order reaction between adsorbed molecular oxygen and adsorbed ammonia (reactions 1-6 below). The rate may be expressed by an equation

$$I_{\text{NO}} = \frac{k_1 k_2 k_3 I_{\text{O}_2} I_{\text{NH}_3}}{(1 + k_2 I_{\text{O}_2} + k_3 I_{\text{NH}_3})^2}$$

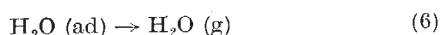
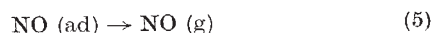
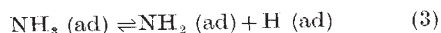
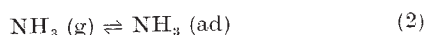
where I is the flux of a species from the surface and k is an exponential function of temperature. The differing temperature coefficients of k_1 (the surface reaction rate constant) and k_2 and k_3 (the adsorption equilibria constants) cause the rate of formation of nitric oxide (at constant reactant fluxes) to pass through a maximum value at a temperature of 850 K. Above this temperature the production of nitric oxide falls because of the fall in the amount of surface covered by adsorbed reactants (Fig. 2 of ref. 1). In conformity with the above rate equation the production of nitric oxide at constant temperature and oxygen flux first increases, then passes through a maximum, and finally falls as the ammonia flux is increased. A similar phenomenon tends to occur when the ammonia flux is fixed and the oxygen flux varied. In this case, however, the weaker adsorption of oxygen on the surface together with an experimental limitation on the maximum permissible molecular flux to the surface made it impossible to observe the maximum in the rate of oxidation except at relatively low temperatures.

At temperatures up to 850 K, the surface oxidation is accompanied by a simultaneous side reaction (reaction 7 below) between adsorbed nitric oxide and adsorbed ammonia which leads to the formation of nitrogen. The rate of this reaction passes through a maximum at a temperature of 700 K. At higher temperatures, smaller adsorption of nitric oxide leads to a reduction in the overall rate of this side reaction.

Above 1,150 K the oxidation is accompanied (particularly at high ammonia flux) by thermal decomposition of ammonia leading to evaporation of species with $m/e=30$ (presumably N_2H_2) from the surface (reactions 8-9 below). Also at temperatures above 1,150 K, adsorbed oxygen tends increasingly to dissociate. These competing processes lead to an overall rate of oxidation which is less than that predicted by the above rate equation.

The processes can be summarized

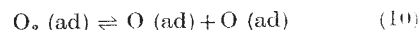
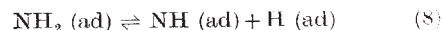
Main oxidation route:



Low temperature side reaction below 800 K:



High temperature side reaction above 1,150 K:



The evaporation of the species with $m/e=30$ was also observed in the complete absence of oxygen, over the same temperature range as in the oxidation process. Because peaks with higher m/e ratios were not detected the species was presumed to be N_2H_2 . Further investigation is necessary to determine whether the process can occur to a significant extent at the higher pressures and somewhat lower temperatures used in commercial converters for the manufacture of nitric acid. Should this be so, the formation of this species could result in the formation of other, more stable but undesirable products, with consequent loss of efficiency.

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¹ Nutt, C. W., and Kapur, S., *Nature*, **220**, 697 (1968).

² Fogel, Ya. M., *et al.*, *Kinetika i Kataliz.* **5**, 496 (1964).

Microbarographic Observation of Acoustic Gravity Waves

It is generally believed that some ionospheric disturbances may be partly caused by the acoustic gravity waves travelling upwards from the troposphere^{1,2}. Wave periods of 5 min to more than 1 h and a narrow spectral band at periods of 7-12 min with a nearly sinusoidal character have been observed^{2,3}. Gossard² discussed various mechanisms of generation of acoustic gravity waves, but the part that convective storms play in this process is not clear. Pierce and Coroniti⁴, emphasizing the circumstantial nature of the evidence on which their proposition was based, proposed that air rising rapidly within a thunderstorm cell overshoots the equilibrium height and is pulled back, resulting in oscillations of the air with a period nearly the same as the local Brunt period. These oscillations occur near the cloudtop levels and generate acoustic gravity waves. They also suggested that, although these waves would be strongly attenuated as they propagated downwards, even at ground level they are significant enough to be detected by microbarographs. The wave oscillations may, however, be obscured by the fluctuations in pressure caused by turbulence created by the formation of the thunderstorm. Fullerton⁵ states that previous studies strongly indicate that sinusoidal pressure variations recorded at the ground are due to tropospheric gravity waves.

We discuss here one such microbarogram resulting from an isolated thunderstorm. The microbarograms obtained at London, Ontario, during the summer of 1967 show several distinct occurrences of periodicities in pressure. The microbarogram of July 1, 1967, is of interest in that it contains a nearly sinusoidal wave of at least three wavelengths with a period of about 8.3 min. The time of arrival of the leading edge is about 0417 GMT.