

The Oxidising Properties of Alumina: the Production of Nitric Oxide

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In recent years the surface properties of alumina have received great attention, particularly the acidity¹ and the oxidising power.² The latter is demonstrated by the discovery in this laboratory that alumina aerogel will, under certain conditions, oxidise adsorbed carbon monoxide to carbon dioxide.³ It has now been found that on heating alumina aerogel which had previously been in contact with moist air, nitric oxide is given off in relatively large quantities.

We examined the gases desorbed when alumina was heated to find out whether either molecular or atomic oxygen was desorbed in significant amounts at temperatures above 300–400°C. The apparatus consisted of a silica tube heated at up to 500°C in a temperature-programmed oven taken from a Perkin-Elmer F.11 Gas Chromatograph. The silica tube contained about 0.25 g. alumina aerogel (γ -alumina, made after the method of Peri and Hannan⁴). Excess of air and water were initially removed by heating at 150°C for up to 3 hours with external vacuum-pumping. The temperature programmer was started to give a heating rate of 3°/min., the tap to the external pumping system was closed, and the gases evolved

were led directly into the ion chamber of an Atlas CH4 mass spectrometer.

The resulting peak heights for nitrogen, nitric oxide, and oxygen are shown in Figure 1 as a function of temperature for a typical sample of alumina aerogel which had previously been heated in air at 600°C for 15 minutes (to remove organic carbon). It will be seen that the predominant peak at temperatures above 150°C is mass 30. This was confirmed as nitric oxide by the absence of any corresponding peaks at masses 44 and 46, the parent peaks of nitrous oxide and nitrogen dioxide respectively.

The samples of alumina used in this work were made in this laboratory from pure materials and at no stage were they in contact with nitric acid or nitrate ions. Nitric oxide could be regenerated by leaving the alumina to stand in the air.

It was found that prior reduction of the alumina with hydrogen suppressed nitric oxide formation almost entirely. The formation of nitric oxide was unaffected by heating the alumina in nitrogen, whereas heating in oxygen suppressed it to a large extent. The empty silica tube which had been used for the experiments gave small but measurable

¹ E. P. Parry, *J. Catalysis*, 1963, **2**, 371.

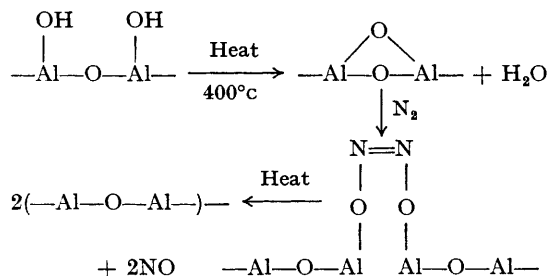
² J. A. N. Scott, B. D. Flockhart, and R. C. Pink, *Proc. Chem. Soc.*, 1964, 139.

³ N. D. Parkyns, paper in preparation.

⁴ J. B. Peri and R. B. Hannan, *Spectrochim. Acta*, 1960, **16**, 237.

amounts of nitric oxide after it had been freshly exposed to the air. This confirms the findings of Kiselev and his co-workers⁵ who obtained nitric oxide by heating silica: some of their samples, however, had been treated with nitric acid beforehand and this treatment might have been a source of nitric oxide on heating.

The mechanism proposed to account for the formation of nitric oxide involves the dehydration of adjacent hydroxyl groups on heating, with the formation of strained oxygen bridges. These are then capable of reaction with nitrogen to form nitric oxide in the reaction scheme below.



The formation of oxide-type free radicals on dehydration is considered less likely because Flockhart, Pink, and Scott² have reported no e.s.r. signals in the examination of alumina treated in this way. It is of interest to note that alumina which had been extensively heated *in*

vacuo until it no longer oxidised adsorbed carbon monoxide, was restored to activity for this reaction by prior addition of a small amount of nitric oxide gas.

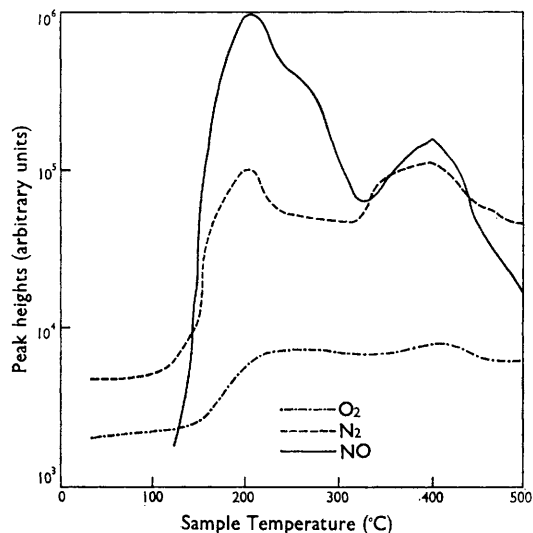


FIGURE 1. Variation of peak heights (arbitrary units) of nitrogen, nitric oxide, and oxygen with sample temperature. Fresh sample of alumina aerogel, rate of temperature rise 3°/minute.

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⁵ A. V. Bondarenko, V. F. Kiselev, and K. G. Krasil'niko, *Kinetics and Catalysis*, 1961, 2, 525.