The removal of oxygen from gas streams: applications in catalysis and gas chromatography

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Abstract Manganese (II) oxide supported on Celite has been found to reduce the oxygen concentration in nitrogen streams to 1 part in $10^{9.5}$, as measured by the resistance of a heated cobalt oxide filament. The supported manganese oxide has been used specifically to protect catalytic materials the properties of which are studied by using them as gas chromatographic columns. Its chromatographic and noncatalytic properties enable it where necessary to be packed directly into such columns.

1 Introduction

The removal of traces of oxygen from other gases is a common experimental and technical problem and many systems have been described in the literature for effecting it (e.g. Brown et al. 1962, Marion et al. 1964, Maak and Sellars 1965 and, for a general review, Shriver 1969). In our case the problem was in a rather extreme form as catalytic reactions were to be investigated in gas-chromatographic columns through which carrier gases, particularly nitrogen, would be passed continuously for periods extending to a week or more. Many of these reactions, for example those occurring on metal surfaces or with organometallic catalysts, are extremely sensitive to very small traces of oxygen. Several dry systems were tested, for example Celite-supported copper, vanadium oxide and chromium oxide – all reduced at 400°C with hydrogen, and from these, supported manganese (II) oxide was found to be the most suitable. Wet systems (e.g. chromium (II) solutions) were excluded as the gases would need subsequent drying and also there are reports that they often introduce other gases (e.g. hydrogen from chromium (II) solution and carbon monoxide from alkaline pyrogallol (Stone 1936)). Manganese (II) oxide coated on vermiculite has been used (Brown et al. 1962) to remove oxygen to 1 part in 2×10^4, but this high residual level is probably a reflection of leakage into the inert atmosphere box especially through the rubber tubing used. Maak and Sellers (1965) using active copper (BTS pellets supplied by BASF) inferred that from practical experience the oxygen pressure was reduced to less than 1 part in 2×10^6, but there were no direct measurements of the oxygen present after treatment. By comparing the efficiency of various metals using the same method of measuring the residual oxygen as we have used (Marion et al. 1964), it was found that the practical limit was fairly constant at 1 part in 10^5, although a value as low as 1 part in 10^9 could apparently be obtained with copper while it still contained hydrogen absorbed in the reduction-activation process.

In our case supported manganese (II) oxide removed oxygen down to 1 part in $10^{9.5}$ which was, as is shown below, the effective limit of the cobalt oxide filament method which was used to measure the oxygen level. The material is self-indicating, changing colour from bright green to brown on absorption of oxygen. It was catalytically inactive under the conditions and for the reactions which were investigated. Supporting manganese (II) oxide on Celite was found to make it more durable and more active: the colour change was also much sharper, being complete in less than 1 mm.

2 Preparation of supported manganese (II) oxide

Manganese acetate was chosen as the starting material for this preparation as it is more soluble in a volatile solvent than the carbonate or the oxalate: the nitrate dissolved in water but gave less satisfactory results. Two parts by weight of hydrated manganese acetate were dissolved in just enough methanol to thoroughly wet one part by weight of Celite (Phasesep N, 60–85 mesh, Phase Separations Ltd). The Celite was added to the solution with shaking and the methanol evaporated overnight at 70°C. The dry powder was resieved (during which much of the manganese acetate was lost) and was packed into a tube and placed in an oven. Nitrogen was passed through it and led from the column out of the window. The temperature of the oven was slowly raised to 400°C, and lowered after two hours when the acetate had completely decomposed to manganese (II) oxide.

The following purification stage was only necessary when the material had to be catalytically inactive. The powder was allowed to oxidize slowly and was then emptied into a flask and heated in air for 4 h at 400°C in order that complete oxidation to manganese dioxide should occur. After cooling, dilute nitric acid was added to remove traces of any other metal oxides and then after 30 min the material was filtered (the filtrate contained iron as was shown by adding thiocyanate). The powder was washed thoroughly with de-ionized water and then dried.

The powder was activated for use by passing hydrogen through a tube containing the sample and the temperature was raised to 400°C by temperature programming at 4°C min^{-1}. The reduction reactions are exothermic and sintering occurs if the temperature exceeds 700°C (White et al. 1962). The active material is pyrophoric in air but provided that sintering is avoided it may be regenerated many times without apparent loss of activity.

3 Measurement of oxygen

To determine the level of oxygen the method of measuring the resistance of a cobalt oxide filament was used (Marion et al. 1964, 1969, Duquesnoy and Marion 1964, Duquesnoy 1965). The method can only be applied to gases which do not reduce the oxide filament to the metal, for example nitrogen but not hydrogen.

A cobalt filament (~ 2 cm long and of 0·25 mm diameter 'spec pure' grade cobalt wire (Johnson Matthey Ltd)) was supported in an oven maintained at 1040°C. Silica tubes were used initially but mullite was later to be more suitable. The oven was controlled by a Foster temperature controller via a 5 A relay switch. The temperature gradient in the oven was measured with a thermocouple (platinum–13% rhodium/platinum) and found to be small but sufficient to create a thermal potential which affected the DC bridge, normally
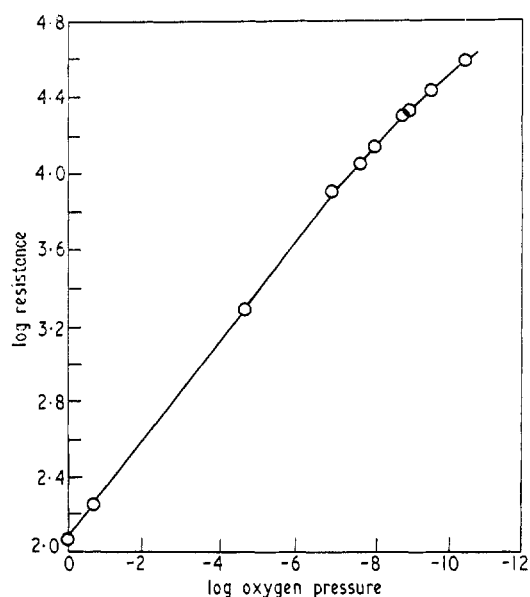
Figure 1 Calibration of cobalt oxide filament. The relation between the logarithm of the resistance (Ω) and the logarithm of the oxygen pressure (atm) is approximately linear, falling off at lower oxygen pressures (Duquesnoy 1964)

used to measure the filament resistance, so that it was necessary to allow for this by reversing the polarity of the filament. The measurements were also checked from time to time with a commercial Wayne–Kerr AC bridge.

The filament was calibrated with suitable mixtures of CO and CO_2 which equilibrate very rapidly at 1040°C to give partial pressures in the required range. At 1040°C, $\Delta G°$ for $2CO + O_2 \cdot \rightarrow 2CO_2$ is $-80 \cdot 350$ kcal, and hence $\log P_{O_2} = 2 \log (P_{CO_2}/P_{CO}) - 13 \cdot 30$, where $\Delta G°$ is the change in standard free energy and P the pressure. The results are shown in figure 1. CO and CO_2 were purified by passing through 13X molecular sieve and then through supported manganese (II) oxide (at room temperature for CO but at 100°C for CO_2 to prevent carbonate formation).

Measurements of the apparent oxygen level in 'dry' nitrogen streams which had been passed through the supported manganese (II) oxide at atmospheric pressure and ambient temperature gave almost invariably a concentration of 1 part in $10^{9 \cdot 5}$. While this has been quite satisfactory for our purpose, it was surprising to find that the figure was so remarkably constant and independent of, for example, gas flow rate. Furthermore, thermodynamic calculations would suggest that the theoretical value for oxygen in equilibrium with MnO and MnO_2 should be of the order of 1 part in 10^{35} at 25°C. These observations may be explained if the resistance of the cobalt oxide filament is eventually determined by the small amount of oxygen produced by dissociation of water vapour at 1040°C. Table 1 shows the correspondence between the measured oxygen pressures and the values calculated on this assumption. It is thus possible that the supported manganese (II) oxide is even more efficient in removing oxygen than it has been possible to demonstrate.

On the other hand, the filament only measures the oxygen level at 1040°C when equilibria involving oxygen, hydrogen and carbon monoxide, etc., have been reached. This means that it is quite possible that the oxygen content of the gas leaving the supported oxide could be higher if it is mixed with the appropriate amount of hydrogen or carbon monoxide

Table 1 Comparison of oxygen pressures calculated

Gas treatment	Oxygen pressure (atm)	
	Calculated†	Observed‡
Dried with 13X molecular sieve (10^{-7} atm H_2O when fresh)	$10^{-8 \cdot 8}$ at 10^{-6} atm H_2O $10^{-9 \cdot 5}$ at 10^{-7} atm H_2O	$10^{-8 \cdot 8} - 10^{-9 \cdot 6}$
Undried (10^{-5} atm H_2O)	$10^{-8 \cdot 2}$	$10^{-8 \cdot 1}$
Passed through water ($2 \cdot 0 \times 10^{-2}$ atm H_2O at 18°C)	$10^{-6 \cdot 0}$ at svp $10^{-6 \cdot 6}$ at svp/10	$10^{-6 \cdot 3}$

† Calculated from water vapour dissociation at 1040°C
‡ Measured after purification of nitrogen with supported manganese (II) oxide

present in the nitrogen. It is difficult to estimate the extent of this effect but it is not considered likely to be dominating. It would require a remarkably constant and exact excess of carbon monoxide over residual oxygen, or of residual oxygen over hydrogen, to produce the measured oxygen pressures, which have varied little from the cylinders of nitrogen obtained at different periods. Furthermore, the inclusion of traps which were highly efficient at removing carbon monoxide had no effect on the observed oxygen pressure at the filament. If the effect should be significant then clearly very low levels of oxygen may be achieved using an oven after the supported manganese (II) oxide, preferably containing a catalyst to equilibrate the reactions of the residual oxygen at a temperature lower than 1040°C.

4 Removal of oxygen from gas stream

Extensive use of the supported manganese (II) oxide was made to remove oxygen from streams of nitrogen used in the catalytic studies. In some experiments there was a continuous flow for over a week or more with no detectable effects of oxygen on the catalysis. This paper is limited to flows in the range from 3 to 300 ml min⁻¹.

The life of the activated material may be followed very easily by the change in colour from bright green to brown. This change occurs very sharply as does the corresponding oxygen pressure. The removal of oxygen (at least to 1 part in 10^8) takes place until the brown zone has reached about 1 mm from the end of the bed. The composition of the exhausted oxide corresponds to about $MnO_{1 \cdot 03}$, presumably meaning that only the surface layers of the oxide are effective. The rate of movement of the brown–green boundary can be used to measure the rate of oxygen uptake, and from this one can deduce the proportion of oxygen in a gas. Thus in one series of experiments, a 26 cm long capillary tube (1 mm inner diameter) was packed with $20 \cdot 8$ mg of the supported oxide material and activated. The rate of oxidation was measured with a flow of nitrogen which contained 1 part of oxygen in $10^{4 \cdot 80}$ parts of nitrogen, as determined by the cobalt oxide filament. The rate of oxidation was then measured with hydrogen for which the cobalt oxide filament cannot be used. The rate of oxidation was found to be slower by a factor of $0 \cdot 91$ from which the oxygen content of the hydrogen was calculated to be 1 part in $10^{4 \cdot 84}$ (figure 2).
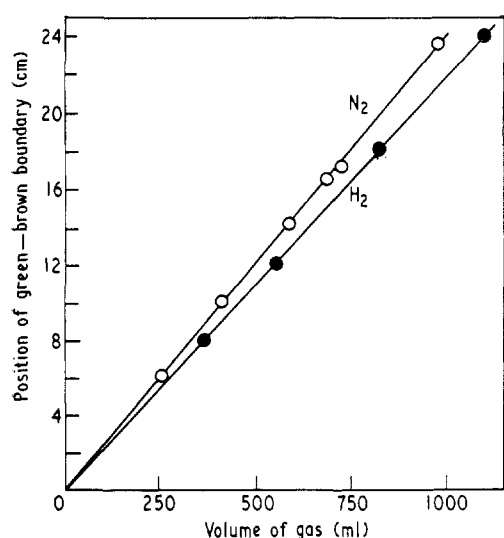
Figure 2 Measurement of the oxygen content of a hydrogen supply by comparison of the rate of movement of the green–brown boundary with the rate found for nitrogen, the oxygen content of which had been determined with the cobalt oxide filament

At the limits of detection set by the filament no oxygen was observed to diffuse through or to be desorbed from the Pyrex tubing or from the Teflon or Viton A seals. Oxygen was found to diffuse through silicone-rubber tubing so that concentrations lower than 1 part in 10^7 could not be obtained. No oxygen was found to diffuse through PVC tubing, but small amounts (corresponding to about 6×10^{-4} ml cm^{-2} internal surface area) were found to desorb initially from PVC tubing which had been exposed to the air.

In general the first symptom of a leak was to observe a flow dependence of the oxygen concentration. When the leak was too small to be detected by the blowing of soap bubbles, it could often be revealed by use of a plastic bag technique. In this, each joint was enclosed in turn by a plastic bag sealed with tape. Nitrogen purified by supported manganese (II) oxide was passed through the bag and if there was a leak at the joint in question the oxygen pressure in the apparatus was quickly reduced. When unpurified nitrogen was then passed into the bag a corresponding rise in the oxygen pressure was recorded. When the leak was deliberately enlarged so that the bag itself was fed from the leak, the effect of the leak on the internal oxygen pressure could be almost eliminated. However some artificial leaks had no detectable effect on the oxygen pressure even though these leaks were large enough to blow soap bubbles. In one case using an artificial leak of approximately 0·2 mm diameter in PVC tubing the rate of oxygen diffusion through the leak fell tenfold when the sun shone on it: this effect was quite reproducible.

At 100°C the supported manganese (II) oxide did not catalyse isomerization or hydrogenation of alkanes, alkenes, alkynes or aromatics nor the dehydration or decarbonylation of alcohols or aldehydes (the methods used would have detected 0·1% reaction). Alkenes were slowly hydrogenated (in hydrogen) over samples of supported manganese (II) oxide which had not been acid washed: the supporting Celite was inert. This activity may well have been due to traces of iron in the manganese acetate. Granular manganese (II) oxide gave strongly tailing chromatographic peaks with hydrocarbon samples at 80°C even after 'anti-tailing' treatment with potassium chloride and hexamethyldisilazine. However with

the supported oxide this tailing was reduced and was found to be negligible for these purposes. Hydrogen was rapidly desorbed on switching the carrier gas from hydrogen to nitrogen.

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