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CHEMISORPTION METHOD FOR THE DETERMINATION AND REMOVAL OF TRACE AMOUNTS OF OXYGEN IN UNREACTIVE GASES

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SUMMARY

An effective purification of carrier gas from trace amounts of oxygen and a simple determination of trace amounts of oxygen in unreactive gases have been achieved with the use of the catalysts Pt/γ-Al_2O_3 and Pd/γ-Al_2O_3.

INTRODUCTION

When using gas chromatography (GC) in physicochemical studies one often needs to remove oxygen effectively from a carrier gas or to determine its concentration in the carrier gas. This is particularly important in determining the dispersion of supported metals. The preparation of a pure metal surface is impossible if the carrier gas contains trace amounts of oxygen, the high reactivity of metal surfaces together with the stability of oxygen compounds explaining the difficulties encountered in the preparation of pure metal surfaces. Oxygen is quickly chemisorbed, in the unactivated process, on the surface of nearly all metals[1] at ambient temperature and a pressure of 10^{-4} mm Hg.

The common method for removing oxygen uses metallic copper at 400–450°. At this temperature the relatively high pressure of oxygen in equilibrium with copper oxide results in a final oxygen concentration of more than 10 ppm. A number of deoxygenating catalysts have been prepared that contain highly dispersed copper on various supports such as SiO_2, Al_2O_3 and molecular sieves[2–5]. These catalysts, commonly used in the temperature range 180–200°, can remove oxygen to the level of *ca.* 1 ppm. In order to reactivate such a catalyst it is reduced[6] with electrolytic hydrogen at 180°. Nickel catalysts are often used for these purposes[7]; oxygen is removed down to 1 ppm, and in some cases to 0.1 ppm (at 70°). Silver catalysts (15 % Ag/Al_2O_3) at 200–300° (refs. 8 and 9), as well as cobalt oxide at ambient temperature[10], have also been used. Recently, Mellwrick and Phillips[11], using manganous oxide supported on Celite, purified nitrogen from oxygen with an efficiency of 1 part per $10^{9.5}$ parts. As the results quoted above equal the oxygen detection sensitivity in the experiments of Mellwrick and Phillips, one can suppose that the oxygen content could be even less. The main advantage of the method is that the colour of the column changes sharply from light green to brown, enabling the process to be controlled.

There are a number of methods for determining the oxygen concentration in gases. Among the most important are colorimetric methods[12,13], the determination of magnetic susceptibility[14], chromatographic methods[15,16] and chemical[17] and electrochemical methods[18,19]. All these methods vary in sensitivity, accuracy, availability and ease of use.

We have used the chemisorption of oxygen, at ambient temperature, on highly dispersed platinum or palladium supported on γ-Al_2O_3, for both purification of oxygen from trace amounts of gases and the determination of trace amounts of oxygen in carrier gases. Both processes are based on the reactions between the platinum or palladium surface and the oxygen in the carrier gas. These reactions, which were used extensively for determining metal dispersion[20,21], proceed according to eqns. 1 and 2,

$$2\,Pt_s + O_2 \rightarrow 2\,Pt_sO \tag{1}$$

$$2\,Pd_s + O_2 \rightarrow 2\,Pd_sO \tag{2}$$

where Pt_s and Pd_s denote the surface atoms of the respective metals.

EXPERIMENTAL

The system used for removing oxygen from the carrier gas is shown in Fig. 1.

The gas, dried on 5A molecular sieves, in column 4, and initially deoxygenated on the catalyst Cu/γ-Al_2O_3, in column 5 at 180°, is finally cleared of oxygen on manganous oxide supported on Gas-Chrom Q or γ-Al_2O_3. The method for the preparation and activation of the manganous oxide catalyst is given in ref. 11. The appa-
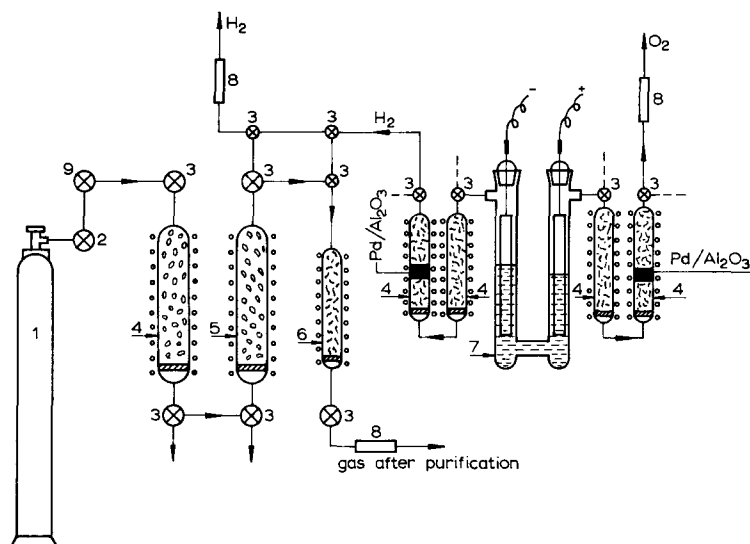

Fig. 1. System for deoxygenation of carrier gas: 1 = source of carrier gas (argon, nitrogen); 2 = pressure-reducing valve; 3 = three-way valve; 4 = columns containing 5A molecular sieves; 5 = column containing catalyst Cu/γ-Al_2O_3; 6 = column containing Mn/Gas-Chrom. Q; 7 = electrolytic system; 8 = flow meter; 9 = fine regulation valve.

ratus also includes an electrolytic system for the generation of hydrogen which is used for the activation of the copper and manganous catalysts. The whole apparatus is made from Pyrex glass; the only rubber connection is between bottle 1 and the rest of the system. The carrier gas flow-rate was 10–250 ml/min and the maximum over-pressure was 2.7 atm.

Oxygen was removed and determined from the stream of carrier gas in the system used previously[6] for the determination of metallic phase dispersion by the pulse chromatographic method (Fig. 2).
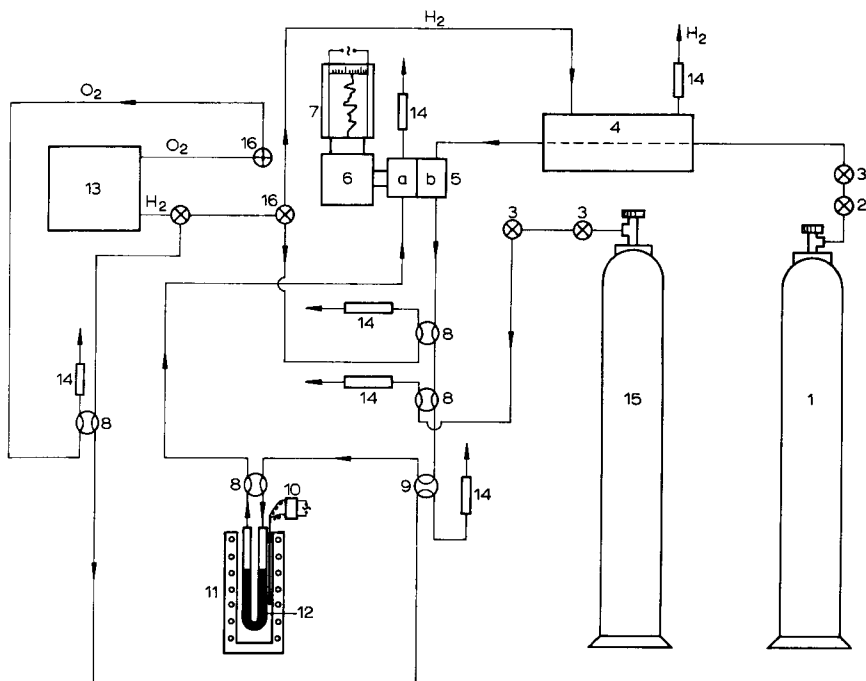

Fig. 2. System for removal and determination of oxygen from a stream of carrier gas: 1 = bottle with unreactive carrier gas (nitrogen, argon); 2 = pressure-reducing valve; 3 = fine regulation valve; 4 = system for deoxygenation of carrier gas (see Fig. 1); 5 = catharometer; 6 = power supply for catharometer; 7 = recorder; 8 = four-way valves; 9 = valve for introducing pulses of oxygen and hydrogen; 10 = thermocouple; 11 = heater; 12 = U-shaped reactor vessel; 13 = electrolytic system (see Fig. 1); 14 = flow meters; 15 = supply of the gas under investigation; 16 = three-way valve.

For oxygen determination the catalysts Pt/γ-Al₂O₃ and Pd/γ-Al₂O₃, prepared by the adsorption method, were used. The metal content was 2–5 %. The temperatures for the initial reduction of the catalysts were 500 and 400° for Pt/γ-Al₂O₃ and Pd/γ-Al₂O₃, respectively. Argon (99.99 %) was used as the carrier gas. It was initially purified from oxygen and water in the system in Fig. 1. After purification it contained less than one part of oxygen in 10^{9.5} parts. For the present investigations, technical nitrogen, pure nitrogen and argon–nitrogen (92:8) and argon–oxygen (55:45) mixtures were used.

RESULTS AND DISCUSSION

The amount of oxygen chemisorbed at ambient temperature on the catalysts $Pt/\gamma-Al_2O_3$ or $Pd/\gamma-Al_2O_3$ is constant and characteristic for a given sample or, more precisely, for a given specific surface of supported metal. Under dynamic conditions processes other than chemisorption (such as physical adsorption or adsorption in the mass) are negligible at ambient temperature.

Since reactions 1 and 2 are very fast and irreversible at ambient temperature, they can be utilized for the quantitative removal of oxygen from the carrier gas and for determination of its concentration. In order to determine the oxygen concentration in the gas under investigation, the amount of oxygen consumed in eqn. 1 or 2 must be known. Let the chemisorption capacity of the catalyst for oxygen be V_{Ch}. If, in time τ, the gas passes through the catalyst with cleared metal surface at a volume velocity F, then some oxidation of the platinum or palladium surface occurs, and τ and F have to obey eqn. 3

$$c_{O_2} \cdot \tau \cdot F < V_{Ch} \qquad\qquad (3)$$

where c_{O_2} denotes the content of oxygen in the gas under investigation. The numerical value of c_{O_2} can be determined by introducing in pulses the additional amount of oxygen, V_d, needed to achieve the value of V_{Ch} for a given mass of catalyst (m_v):

$$c_{O_2} = \frac{V_{Ch} - V_d}{\tau \cdot F} \qquad\qquad (4)$$

Determination of V_{Ch}

In the chemisorption method for metal-dispersion determination, V_{Ch} denotes the maximum amount of oxygen chemisorbed on a clean surface of metal. The clean surface of platinum in the $Pt/\gamma-Al_2O_3$ catalyst was prepared as follows. The sample of catalyst (2–7 g), containing 2–5% of platinum, was placed in reaction vessel 12 (Fig. 2) and heated to 500° in a stream of pure carrier gas. After 1 h the catalyst was reduced for 1 h with electrolytic hydrogen (volume velocity, *ca*. 20 ml/min). One hour after the reduction, the catalyst was "rinsed" with pure argon (volume velocity, *ca*. 40 ml/min) and cooled to the ambient temperature. In the case of the $Pd/\gamma-Al_2O_3$ catalyst, the procedure for clean-surface preparation was the same, exept that reduction was carried out at 350–400°.

Then, by introducing small pulses of oxygen (*ca*. 0.1 ml), using valve 9 (Fig. 2), into the stream of carrier gas, the value of V_{Ch} was determined from the number of sorbed pulses. If, for the first unsorbed pulse, the recorded peak is smaller than the following peak, one has to include an appropriate correction. The volume of oxygen introduced in one pulse was determined to an accuracy of 0.1% by calibration with mercury.

Determination of oxygen in an unreactive gas

A stream of the gas under investigation was passed through the sample of catalyst, prepared as described above at a volume velocity in the range 10–150 ml/min.

TABLE I

VALUES OF OXYGEN CONCENTRATIONS IN GASES

V_i = Volume of injected pulse of gas under investigation; n_i = number of pulses; $V_g = V_i \cdot n_i$ = total volume of gas; m_p = weight of catalyst sample.

Gas investigated	m_p (g)	c_{pt} (%)	V_{Ch} (ml)	F (ml/min)	τ (min)	V_d (ml)	c_O^- (%)	V_i (ml)	n_i	V_g (ml)
A. Nitrogen*	0.358	2.78	0.078	150	120	$6.05 \cdot 10^{-2}$	$9.78 \cdot 10^{-5}$			
					150	$5.63 \cdot 10^{-2}$	$9.69 \cdot 10^{-5}$			
					300	$4.35 \cdot 10^{-2}$	$9.91 \cdot 10^{-5}$			
							$9.79 \cdot 10^{-5}$			
B. Argon–nitrogen (92:8)	1.545	2.78	0.337	50	25	0.238	$7.92 \cdot 10^{-3}$			
					45	0.155	$8.09 \cdot 10^{-3}$			
					65	0.073	$8.12 \cdot 10^{-3}$			
							$8.04 \cdot 10^{-3}$			
C. Nitrogen	5.015	2.78	1.094	10	5	0.940	0.308			
					10	0.792	0.302			
					15	0.626	0.312			
					20	0.460	0.317			
					25	0.219	0.310			
					30	0.176	0.306			
							0.309			
D. Argon–nitrogen (55:45)	5.015	2.78	1.094			1.005	44.5	0.1	2	0.2
						0.913	45.3	0.1	4	0.4
						0.825	44.8	0.1	6	0.6
							44.9			

* After deoxygenation on Cu/γ-Al₂O₃.

Oxygen is chemisorbed and the gas passing through the catalyst is effectively purified from oxygen provided eqn. 3 holds true.

Determination of V_d

The additional amount of oxygen, V_d, needed to achieve V_{Ch} is determined by reintroducing the sample used in the determination of oxygen in an unreactive gas into the stream of pure gas and repeating the procedure described for V_{Ch}. Numerical examples are presented in Table I.

In Table IA are given the results of the oxygen content of nitrogen which had previously been purified by deoxygenation on a Cu/γ-Al₂O₃ catalyst. Before purification the oxygen content in the gas was *ca.* 0.31 % (see Table IC). After purification, the concentration of oxygen was *ca.* $9.8 \cdot 10^{-5}$%. The relatively long time needed for exposure (several hours) was the only disadvantage of these measurements. For a given sample of catalyst, reduction of the reaction time would be possible if the velocity of carrier gas were higher. A velocity of *ca.* 250–300 ml/min would seem to be the limit for this kind of experiment.

In Table IB and IC are given the results for gases with oxygen concentrations smaller than 1 %. In Table ID are given the results of oxygen concentrations for the mixture argon–oxygen (55:45). Because of the high oxygen content, it was not possible to pass the gas continuously through the catalyst. In these measurements we injected the investigated mixture, the injected volume being 0.1 ml.

In all cases the variation in the results was within $\pm$ 2 % of the average value. As seen from Table I, gases with very different amounts of oxygen can be investigated by means of this method.

The chemisorption method for oxygen determination in unreactive gases (nitrogen, argon, helium, krypton) is efficient if the gases under investigation are free from carbon monoxide, hydrogen, vapours of hydrocarbons and sulphur-containing compounds. This limitation is because of the high reactivity of clean surfaces of platinum or palladium. If the above gases are present they interfere with oxygen chemisorption. Cases in which the concentrations of the above gases are comparable to the oxygen concentration are rare, and the gases have to be removed before oxygen determination.

The capacity of a catalyst is limited by the maximum chemisorption capacity of the given sample for oxygen, V_{Ch}. The value of V_{Ch} can be increased by increasing the mass of the catalyst or by increasing its metal content. However, the use of samples greater than 10 g or of catalysts containing more than 5–7 % of metal is troublesome experimentally. Besides, increased metal content decreases its dispersion, *i.e.* by decreasing the value of V_{Ch} in relation to the unit of metal mass. If one uses, for example, 5 g of the catalyst Pt/γ-Al_2O_3 containing 5 % of metal with a dispersion of 0.4, the value of V_{Ch}, determined according to eqn. 1, is *ca.* 6 ml of oxygen. For Pd/γ-Al_2O_3, under the same conditions, V_{Ch} is *ca.* 10 ml. Such a sample of catalyst can be used for purifying quite a large volume of carrier gas provided the oxygen concentration is sufficiently low.

Consider the equilibrium between the metals, their oxides and oxygen according to eqn. 1 or 2. The dissociation pressure of the oxide is the reciprocal of the equilibrium constant, and it can be seen that the dissociation pressure, p, is given by eqn. 5

$$p = \exp (E_A/RT) \tag{5}$$

where E_A is integral heat of adsorption and R and T have their usual meanings. For platinum and palladium the integral heats of oxygen adsorption are -67 kcal/mol, which corresponds to a dissociation pressure of *ca.* 10^{-13} torr. One can thus deduce that the sensitivity of the method proposed above could be equal to about one part of oxygen in 10^{16} parts of unreactive gas. This limit, however, cannot be achieved practically because of the limited sensitivity of the measuring system.

For an oxygen content of lower than 1 %, the gas under investigation should be introduced continuously into the system, while for an oxygen content of greater than 1 % the pulse method should be used (see Table ID). The same sample of catalyst can be used many times for oxygen determination; the only condition consists in purification of the metal surface. The presented method is simple and easy to carry out in laboratories in which the dispersion of metals is determined by chromatographic methods. It requires, however, a very pure carrier gas (*i.e.*, a good purifying system) for the determintion of the value of V_{Ch} and for the purification of the catalyst.

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