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An Inspection of the Purity of Helium Used as the Carrier Gas in Pulse-adsorption Experiments

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Synopsis. A novel method is proposed to inspect the oxygen content of the helium used as the carrier gas in pulse-adsorption experiments. The oxygen is first adsorbed on Pt/SiO_2 catalyst and then titrated by CO pulses. This method is very simple and requires only a conventional pulse-adsorption system.

The measurement of the metal surface area —dispersion— of supported metal catalysts is one of the most important techniques in the characterization of catalysts. The selective chemisorption of such gases as hydrogen, carbon monoxide, and oxygen is very frequently used for this purpose. This method is, however, based on the correspondence of the numbers of surface atoms and adsorbed molecules, and so the stoichiometry of chemisorption must be stable. Hydrogen chemisorption is believed to be most satisfactory[1] because the stoichiometry is stable for many metals, even when the dispersion is relatively high. On the other hand, CO adsorbs on noble metals very rapidly and attains the equilibrium of adsorption very easily at room temperature because of its strong affinity to metals, although the stoichiometry is sometimes complex.[2] Such behavior of CO is very advantageous for chemisorption using a pulse appararus, which is a very simple and convenient method of chemisorption. Thus, hydrogen adsorption is preferred by laboratories doing basic research, whereas CO adsorption is often selected by the researchers of catalysts for practical applications.

One of the most serious technical problems which we encounter when we try to perform pulse-adsorption experiments is that a very high purity is required for the carrier gas. For example, if helium carrier gas contains 1 ppm of oxygen and is passed through a Pt/SiO_2 catalyst (0.1 wt% Pt, 0.3 g) at a rate of 30 ml/min for 1 h (the time required to desorb H_2 and to cool it down to room temperature after pretreatment), then the number of oxygen atoms adsorbed on the catalyst surface is 10% of the total Pt atoms. Therefore, the oxygen content of helium must be less than 0.1 ppm for exact experiments. Obviously, it is important to inspect whether or not the carrier gas has a purity high enough of satisfy the demand. However, it is not easy to determine such a very low concentration of oxygen. Because the advantage of using the pulse-adsorption of CO is convenience, the inspection of the carrier gas is of no value unless the method is also very simple and convenient.

The reason why such a high purity of the carrier gas is required is that the reduced metal surface has a strong function to capture gaseous oxygen. Therefore, we tried to determine the oxygen content by utilizing the ability of metal catalysts to capture oxygen; *i.e.*, first flowing the carrier gas through a Pt catalyst to collect the small amount of oxygen on the Pt surface, and second analyzing the adsorbed oxygen by means of O_2–CO titration.

This method is based on the following surface reactions on supported Pt catalysts;[3]

$$1/2\cdot O_2 + Pt(s) \rightarrow Pt\text{-}O(a), \tag{1}$$

$$2CO + Pt\text{-}O(a) \rightarrow Pt\text{-}CO(a) + CO_2, \tag{2}$$

$$CO + Pt(s) \rightarrow Pt\text{-}\ CO(a). \tag{3}$$

When the carrier gas is passed through the Pt catalyst for a period longer than in the pulse-adsorption experiment, the gaseous oxygen contained in the helium is captured on the Pt surface as in Eq. 1. The adsorbed oxygen easily reacts with CO pulses at room trenperature, and CO_2 is evolved following Eq. 2, so we can estimate the amount of adsorbed oxygen by measuring the amount of CO_2. If the Pt surface is only partly covered with oxygen, Reaction (3) also takes place on the surface. Because Reaction (2) occurs in preference to Reaction (3), CO_2 is easily detected, even if its amount is small.

Figure 1 illustrates the apparatus. Helium was purified by being passed through a reduced copper trap (500 K) and molecular sieves. CO was pulsed by means of a six-port valve with a sampling tube of 0.352 ml attached. This apparatus is similar to a conventional pulse-adsorption system except that an active carbon column is attached between the sample

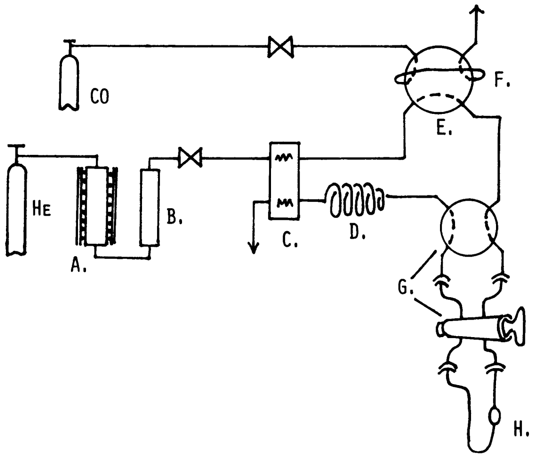

Fig. 1. Experimental apparatus both for purity check of carrier gas and pulse adsorption of CO. A. Oxygen trap (activated copper; normally kept at 500 K), B. Water trap (molecular sieves), C. Detector, D. Active carbon column, E. 6-port valve, F. Sampling tube, G. 4-port valve, H. Catalyst sample.

and the detector in order to separate the CO and CO_2. After the carrier-gas inspection is finished, experiments on CO adsorption or O_2–CO titration may be carried out using this apparatus unchanged.

The probe catalyst, Pt/SiO_2, was prepared by impregnating SiO_2 (aerosil 380) with an aqueous solution of hydrogen chroloplatinate(IV). The metal loading was 0.15 mmol/g (2.8 wt%). The pretreatment procedure was the same as in our previous studies of O_2–CO titration over Pt-Ru/SiO_2.[3,4] That is, after the catalyst had been evacuated at room temperature for 10 min, it was heated to 400 K and then evacuated for 1 h. In a flow of hydrogen, the temperature was increased to 600 K at a rate of 10 K/min. The catalyst was subsequently reduced at 600 K for 3 h, evacuated at 720 K for 30 min, and then cooled slowly to room temperature. After the pretreatment, the reactor was removed from the pretreatment apparatus to the pulse apparatus, keeping a vacuum. Such a pretreatment minimized the period (less than 30 min) during which the catalyst was in contact with the carrier gas compared with the case of desorbing hydrogen in a flow of helium.

Figures 2-A and B show typical examples of chromatograms resulting from this experiment. When the heating of reduced Cu was stopped and helium was passed through the catalyst without removing the oxygen for 1 h, we obtained the chromatogram shown in Fig. 2-A. CO was consumed almost completely in the first three pulses. A significant amount of CO_2 was evolved in the first pulse, but only a trace was evolved in the following pulses. Residual CO was detected after the fourth pulse. Because CO_2 is evolved as a single peak, as a result of the character of the Pt surface in preferring Reaction (2) to Reaction (3), it is easy to determine CO_2 even when the amount is very small. In this case, the oxygen content of helium was concluded to be 9.7 ppm.

When the Cu trap was working at 500 K, and when the system was in the same condition as in the CO adsorption experiments, we obtained the chromatogram shown in Fig. 2-B. In this case, no evolution of CO_2 was observed after the helium had flowed for 1.5 h. Supposing the peak height of CO_2 to be less than 1 mm (the same order as the baseline perturbation), the oxygen content of helium was calculated to be less than 0.1 ppm. Such a calculation is based on the assumption that all of the oxygen molecules are captured on the Pt surface. However, when the oxygen content is very low, the adsorption of oxygen (Reaction (1)) may be reversible and not all the oxygen may be captured. Thus, this method may be incomplete as a means of determining the oxygen content. Even so, it is sufficient as a means to judge whether or not the carrier gas is pure enough for pulse-adsorption experiments, because if the oxygen concentration is so small that oxygen is not captured on the metal surface, then the impurity can not affect the CO-adsorption experiments.

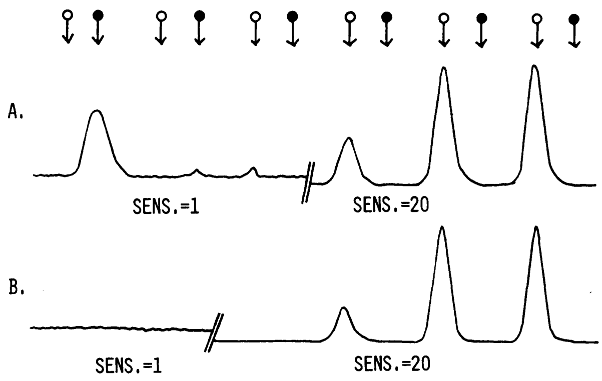

Fig. 2. Examples of chromatograms resulting from the CO titration of adsorbed oxygen contained in the helium carrier gas. ○: CO, ●: CO_2.

A. Heating of oxygen trap was stopped, B. Oxygen trap was kept at 500 K.

In this way, we could estimate the effect of oxygen impurity in the carrier gas on CO adsorption using a conventional pulse-adsorption system with quite a simple procedure.

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