BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 634—635 (1972)

Gas Chromatographic Determination of Reversible Adsorption of Hydrogen. XI.[1] Reversible Adsorption of Hydrogen over Some Metal Oxides

Yoshiko SHIGEHARA and Atsumu OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku, Tokyo

(Received July 5, 1971)

It has been shown that the rapid and reversible part of hydrogen adsorption can be measured by means of the gas chromatographic retention volume of deuterium in hydrogen carrier. This method has been applied to metals[2] and metal oxides.[3] It was found that the rapid and reversible adsorption of hydrogen is molecular at low temperature and atomic at higher temperatures. However, not many oxides can remain as oxide at high temperature in a hydrogen stream. The reversible adsorption of hydrogen was determined over some hardly reducible oxides at higher temperatures.

Experimental

The apparatus and procedure for gas chromatographic measurement were essentially the same as before.[2] A deuterium sample was introduced into the hydrogen carrier gas by means of a doser made of glass tubing, and was passed to the catalyst column and detecter.

Vanadium trioxide was obtained from Mitsuwa Chemicals Company, Limited. Chromia was prepared by thermal decomposition of ammonium dichromate. Manganous oxide and zinc oxide were prepared by thermal decomposition of manganous carbonate and zinc oxalate *in vacuo*. The gas chromatographic columns of these oxide samples were made from a glass U tube 10—20 mm in diameter. The amount of samples were as follows. The oxide sample was *in situ* pretreated with hydrogen at rising temperature up to 500°C, during which treatment the following amounts of hydrogen were absorbed as below.

Cr_2O_3	V_2O_3	MnO	ZnO
9.0 g	24.7 g	46.8 g	17.8 g

Results and Discussion

1. Chromia. The deuterium retention volumes are shown in Fig. 1 as a function of temperature. The isobar is independent of the direction of temperature variations. It appears that there is an activated adsorption of hydrogen starting from around 100°C.

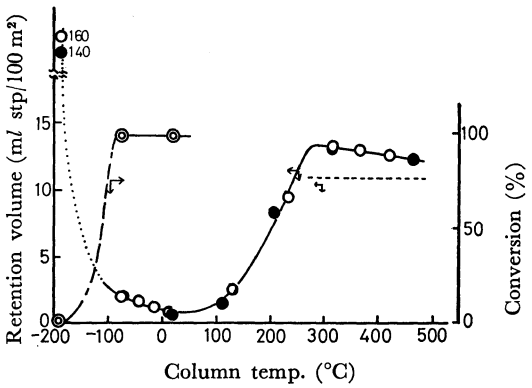

Fig. 1. Deuterium retention volumes and conversion of D_2 into HD by reduced chromia (9.0 g) at different temperatures.
—○— rising temperatures from −195 to 460°C,
—●— lowering temperatures from 460 to −195°C,
—◎— conversion of D_2,
------ difference between retention volume and activated adsorption.

Oxide	Cr_2O_3	V_2O_3	MnO	ZnO
Sorbed hydrogen	18 ml/100 m²	*ca.* 80 ml/g[a]	*ca.* 10 ml/100 m²	14 ml/100 m²
Color of oxide after H_2 treatment	gray	black	pale green	gray

a) This amont of hydrogen corresponds to 0.5 mol per mol of V_2O_3. However, X-ray analysis of hydrogen-treated sample showed only V_2O_3. The large amount of hydrogen consumed might be due to excess oxygen involved.

1) Part IX: Ref 3b, Part X: Ref 3c.

2) A. Ozaki, F. Nozaki, K. Maruya, and S. Ogasawara, *J. Catal.*, **7**, 234 (1967); A. Ozaki, Y. Shigehara, and S. Ogasawara, *ibid.*, **8**, 22 (1967); Y. Shigehara and A. Ozaki, *Nippon Kagaku Zasshi*, **88**, 838, 844 (1967), *J. Catal.*, **10**, 183 (1968), **15**, 224 (1969).

3) Y. Shigehara, and A. Ozaki, a) *ibid.*, **21**, 78 (1971); b) *Nippon Kagaku Zasshi*, **91** 940 (1970); c) *ibid.*, **92**, 297 (1971).

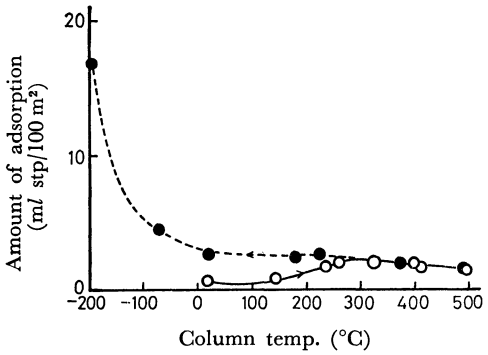

Fig. 2. Hydrogen adsorption isobar on reduced chromia.
—○— 20 → 500°C, —●— 500 → −195°C

In order to examine the contents of the deuterium retention, the static adsorption measurements were carried out on the same sample. The results are shown in Fig. 2. The activated adsorption of hydrogen is clearly demonstrated, but the amount is much less than that of deuterium retention. There must be another type of surface hydrogen which is incorporated into the deuterium retention through an exchange reaction. The amount of exchangeable hydrogen can be estimated by subtracting the activated adsorption from the deuterium retention. It is independent of temperature and is shown in Fig. 1 by the dotted line. Thus the exchangeable hydrogen would be the hydroxyl hydrogen. More than 80% of the deuterium retention accordingly seems to be caused by the surface hydroxyl.

The extent of conversion of D_2 into HD is 100% at above −75°C, while the activatedly adsorbed hydrogen is isotopically equilibrated with the flowing hydrogen above 300°C as shown in Fig. 1. This suggests that the exchange reaction between H_2 and D_2 is catalyzed by an active site other than the adsorption site for high temperature adsorption.

2. Vanadium, Manganese and Zinc Oxides. Three kinds of measurements were made on these oxides, for which activated adsorption of hydrogen is known.[4]

(1) Retention volume of deuterium sample.

(2) Extent of conversion of D_2 into HD in an eluted pulse.

(3) Static measurements of adsorption isobar of hydrogen (summarized in Fig. 3).

The retention volumes over these oxides are commonly null near room temperature, but increase above

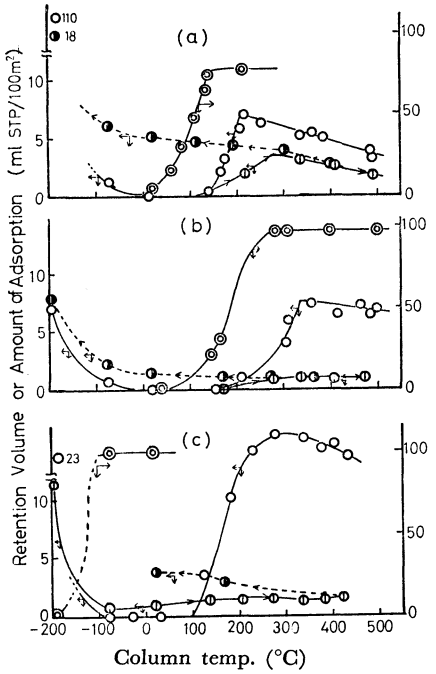

Fig. 3. Deuterium retention volume, amount of adsorption of hydrogen and conversion of D_2 into HD on vanadium (a), manganese (b) and zinc oxides (c).
Retention volume, —○—
Amount adsorbed, —◑— (rising temperature)
—◑— (lowering temperature);
Conversion, —◎—.

about 100°C up to respective maximums. In higher temperature ranges where the retention volumes decrease with rise in temperature, the rate of adsorption and exchange reaction would be fast enough to establish an isotopic equilibrium between gas and solid surfaces.

The extent of conversion of D_2 into HD begins to increase and reaches isotopic equilibrium[5] at a much lower temperature than the retention volume, particularly in the case of zinc oxide, where the conversion is 100% below 0°C. Thus the exchange reaction between H_2 and D_2 seems to be catalyzed by an active site other than the adsorption site for the high temperature adsorption.

The difference between the retention volume and the static adsorption must be due to the isotopic exchange between the adsorbed hydrogen and surface hydroxyl. The exchange is most extensive in the case of zinc oxide.

4) K. Tarama, and S. Teranishi, *Kogyo Kagaku Zasshi*, **55**, 316 (1952); H. S. Taylor, A. T. Williamson, *J. Amer. Chem. Soc.*, **53**, 2168 (1931); H. S. Taylor, S. C. Liang, *ibid.*, **69**, 1306 (1947). V. Kesavulu and H. A. Taylor, *J. Phys. Chem.*, **64**, 1124 (1960).

5) The equilibrium conversion to HD was lower than 100% in the case of V_2O_3 because of the small volume of the sample column of oxide.