THE POISONING EFFECTS OF WATER VAPOR ON THE ADSORPTION OF CARBON DIOXIDE BY MANGANESE DIOXIDE

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Manganese dioxide, when pure, catalyzes the reaction between carbon monoxide and oxygen to form carbon dioxide. Water vapor is a strong poison for this reaction, making the oxide inactive.[1] It has been shown that water is adsorbed by manganese dioxide and that, when the pressure is less than about four-tenths the saturation value, the adsorption is a surface phenomenon.[2] Water vapor must retard the oxidation of carbon monoxide by covering a part of the surface of the oxide which is available for the adsorption of the reacting gases. The present paper deals mainly with the effects of the presence of water on the adsorption isotherms of carbon dioxide on manganese dioxide at 25°.

Materials, Apparatus and Experimental Procedure

The manganese dioxide used is from the lot prepared and used in previous work.[2] Carbon dioxide, from a tank, was dried by passing through concentrated sulfuric acid and over phosphorus pentoxide.

The apparatus used for determining the adsorption isotherms was of the constant volume type.[3] A small bulb of known volume (20–22 cc.), containing the oxide, was connected to a forevolume of known capacity. Gas at a known pressure and temperature in this forevolume was allowed to expand into the adsorption bulb. The oxide adsorbed the gas and the pressure decreased. The pressure decrease was a measure of the amount of gas adsorbed, if correction were made for expansion of the gas into the adsorption bulb. The changes in temperature in the forevolume were noted, the appropriate corrections being applied for these variations.

The apparatus was constructed of pyrex glass. The adsorption bulb was maintained at 25° by means of a large water thermostat. The forevolume contained a McLeod gage, a U-tube for measuring pressures above 2 mm., a bulb of suitable size, and connections to the vacuum pumps and gas generating system. The mercury in the U-tube and McLeod gage was maintained at fixed levels. When the mercury was at these levels, the capacity of the forevolume was known from previous calibration by means of mercury or water.

About 4 g. of manganese dioxide was weighed into the adsorption bulb and, in all experiments, then heated at 190 ± 3° for three hours under the vacuum produced by a mercury pump backed by an oil pump. The oxide was cooled and immersed in the thermostat. The gas under investigation was admitted to the forevolume and its pressure and temperature noted, after the system had been swept out several times. This gas was admitted to the oxide and its pressure and temperature determined at regular time intervals until the pressure attained a constant value. This was taken as the equilibrium point. The stopcock to the adsorption bulb was closed, more gas

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[1] Rogers, Piggot, Bahlke and Jennings, THIS JOURNAL, 43, 1973 (1921); Whitesell and Frazer, ibid., 45, 2841 (1923); Lamb and Vail, ibid., 47, 123 (1925).

[2] Foote and Dixon, ibid., 52, 2170 (1930).

[3] See, for example, Hoskins and Bray, ibid., 48, 1454 (1926).

admitted to the forevolume, and the next equilibrium point measured in the same way as before.

The surface of the oxide was poisoned with a known amount of water as follows. The forevolume was filled with water vapor up to any desired pressure and its temperature recorded. Connection with the oxide, which had just been outgassed, was made and the vapor was adsorbed, leaving a negligible amount in the gas space. It was necessary to repeat this process several times whenever the amount of water desired corresponded to a pressure in the forevolume greater than the vapor pressure at room temperature.

The weight of outgassed oxide has been used to calculate the amount of gas adsorbed per gram of oxide. In previous work[2] the weight of oxygen and water lost by a sample of oxide during heating was determined by direct weighing. The mean of thirteen experiments showed that the loss in weight was practically constant and equivalent to 0.0379 g. per gram of original oxide. The volume of the adsorption bulb was corrected for the volume of the outgassed oxide, the specific volume of the oxide being taken as 0.2168 cc. per gram.[4]

The equilibrium pressure extended from 3 to 500 mm. of mercury. Since the object was to compare the isotherms for a poisoned and unpoisoned oxide, no attempt was made to read the pressures closer than 0.1 mm. The largest capacity of the forevolume was 821 cc. and the pressure changes in this volume were never less than 5 mm. The results given in the following sections are accurate to 4% or better.

The Adsorption Isotherms of Carbon Dioxide

The capacity of the forevolume in the experiments was 821 cc. The adsorption isotherms of this gas on manganese dioxide at 25° are plotted in Fig. 1, v/m as ordinate and p as abscissa. v/m is the number of cubic centimeters of carbon dioxide, reduced to 0° and 760 mm. pressure, adsorbed per gram of outgassed oxide, and p is the equilibrium pressure in millimeters of mercury. Curve 1 represents the isotherm for an oxide unpoisoned with water vapor. The amount of water necessary to cover the surface of one gram of oxide at 25° we assume is approximately 0.063 g. This assumption is based on the adsorption isotherm of water on manganese dioxide at this temperature.[7] The weight of water used to poison the oxide of Curve 2 was 0.0096 g. per gram of oxide, or 15% of the surface was covered. In Curves 3 and 4, 34 and 38% of the surfaces were covered, respectively.

The results show that when approximately 35% of the surface is covered with water vapor, the amount of carbon dioxide adsorbed is reduced by about 50%, the effect being more pronounced at lower pressures. This is a strong indication of the presence of active adsorption patches on the oxide. Since the water covers these patches, the adsorption of carbon dioxide shows a greater decrease than we would expect from the fraction of the surface poisoned.

The small amount of water used in these experiments is adsorbed so completely from the vapor phase that it is very unlikely that carbon dioxide can displace it from the solid to a measurable extent. If it were displaced,

[4] Draper, THIS JOURNAL, **50**, 2637 (1928).

however, the surface covered by water vapor would be less than calculated without decreasing the partial pressure of carbon dioxide proportionally and the effect would be even more pronounced than stated above.

Two check runs in the absence of water vapor agree with Curve 1. The adsorption and desorption curves nearly coincide at all pressures. The time necessary to attain equilibrium was ten minutes, although readings were taken over a period of one hour. The manganese dioxide of Bray and Hoskins[3] adsorbed only about half the amount of carbon dioxide that we have found for our sample of manganese dioxide, the attainment of equilibrium was slower, and adsorption somewhat irreversible.
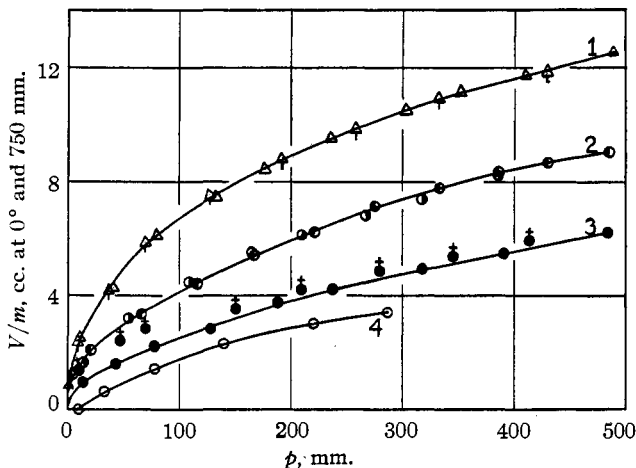

Fig. 1.—Effect of water on the adsorption isotherms of carbon dioxide on manganese dioxide at 25°. % of surface poisoned with water: 0 %, △ adsorption, ⩑ desorption; 15%, ◖ ads., ◖ des.; 34%, ● ads., ● des.; 38%, ○ ads.

The Behavior of Carbon Monoxide toward Manganese Dioxide Containing Adsorbed Water.—It is well known that carbon monoxide reacts with manganese dioxide at room temperature to form carbon dioxide and the latter may then leave the surface.[5] However, the carbon monoxide may form manganese carbonate or, after reaction, the carbon dioxide formed may remain in the form of the carbonate.[6] Whether this behavior is to be classed as true adsorption may be questioned. The isotherms have the general form of adsorption isotherms, however, and we shall so refer to them. Since the system carbon monoxide–manganese dioxide is so complicated, we shall report only qualitative results, in which it has been assumed that the decrease in pressure in the forevolume is a measure of the carbon monoxide adsorbed. The carbon monoxide used in the experi-

[5] Benton, THIS JOURNAL, **45**, 887 (1923); Hoskins and Bray, Ref. 3.

[6] Frazer and Greider, *J. Phys. Chem.*, **29**, 1099 (1925).

ments was prepared by dropping formic acid into concentrated sulfuric acid. It was then purified by passing it over solid potassium hydroxide, through concentrated sulfuric acid and over phosphorus pentoxide.

The adsorption and desorption isotherms of carbon monoxide at 25° were determined for samples of oxide poisoned and unpoisoned with water vapor. The pressure did not attain a constant value, after any new addition of gas, even at the end of four hours, but this further decrease in pressure was slow. Four to five hours were allowed for the system to reach this nearly steady state which was taken as an arbitrary equilibrium point.

The isotherms are highly irreversible, about 50–60% of the gas being retained very strongly by the oxide. The adsorption isotherms are of the same shape as those for carbon dioxide (see Fig. 1), but the amount of carbon monoxide adsorbed is approximately twice as great for the same pressure. The adsorption on a surface of oxide poisoned with water vapor is similar to that of carbon dioxide, especially below 250 mm. pressure. That is, the first fraction of the surface poisoned causes the greatest lowering of adsorption. Further poisoning decreases the adsorption, but by no means in a strictly proportional manner.

Summary

The adsorption isotherms at 25° of carbon dioxide on manganese dioxide with and without adsorbed water have been determined. The adsorption is reversible. Water reduces the adsorption markedly. The results indicate the presence of "active adsorption patches" on the oxide surface since the first portion of water adsorbed results in the greatest lowering of the carbon dioxide adsorbed.

The corresponding behavior of carbon monoxide toward manganese dioxide with and without adsorbed water is more complicated. Adsorption is highly irreversible, but the presence of adsorbed water causes the same qualitative effect that it does with carbon dioxide.

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