MOLECULAR AND ACTIVATED ADSORPTION OF CARBON MONOXIDE ON MANGANOUS OXIDE SURFACES

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During the course of a thorough experimental study of the adsorption of hydrogen on oxides of manganese,[1] an orientation experiment indicated that carbon monoxide behaved in the same general way as hydrogen. The purpose of this communication is to report the results of a comprehensive investigation leading from the earlier observation, and to compare the results obtained with the two gases.

The general theory underlying the experimental work has been given by Taylor,[2] whose paper should be consulted for a comprehensive background. Experimental studies of the adsorption of carbon monoxide on various oxides have been carried out by many,[3] although none of these workers chose the particular surfaces used in this investigation.

Experimental

The preparation of the catalysts and the apparatus was described in the earlier paper.[1] The carbon monoxide used for these investigations was prepared by dropping formic acid into concentrated sulfuric, passing the resulting gas through copper gauze held at 300°, ascarite and phosphorus pentoxide.

Low Temperature Adsorption.—Isothermal adsorption was measured at the temperature of liquid air and again at −78.5°. The results are given in the following tables, which show the amount of carbon monoxide adsorbed in cubic centimeters per gram of catalyst, and which give the resulting equilibrium pressures in millimeters of mercury. All gas volumes were reduced to standard conditions. The general procedure consisted in the preliminary evacuation of the catalyst at 450° and the immersion of the catalyst tube in the desired thermostating medium for several hours to facilitate the attainment of temperature equilibrium. Successive portions of carbon monoxide were then added, readings of the equilibrium pressure being made after each addition. When several points had been obtained desorption was carried out in the same way. The reversibility of an isotherm is shown by the fidelity with which adsorption and desorption points fall on a common curve. In all cases low temperature adsorption was instantaneous.

[1] Taylor and Williamson, THIS JOURNAL, 53, 2168 (1931).

[2] H. S. Taylor, ibid., 53, 578 (1931).

[3] See for example Benton, ibid., 45, 887 and 902 (1923); Taylor and Kistiakowsky, ibid., 49, 2471 (1927); Markham and Benton, ibid., 53, 497 (1931); Lazier and Adkins, J. Phys. Chem., 30, 356 (1926); Schmidt, Z. physik. Chem., 133, 265 (1928); Garner and Kingman, Nature, 126, 352 (1930).

In addition to the thermostating agents described in a previous paper, use has been made of liquid air, whose temperature could be read continuously by an oxygen vapor pressure thermometer.[4] It was found that an isotherm could be completed in such a bath with a total temperature drift of less than 0.5°.

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TABLE I

ISOTHERMS ON 51.3 GRAMS OF MnO–Cr$_2$O$_3$

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| Temp., 85.0°K. | | 85.0°K. | | 194.5°K. | |
P	V ads./m.	P	V ads./m.	P	V ads./m.
0	0.0	32	18.0	0	0.00
1	8.8	58	19.2	6	2.63
2	10.4	87	20.5	20	3.65
3	12.2	118	21.6	62	4.52
4	13.2	91	20.8	132	5.18
5	14.2	68	19.9	227	5.70
8	15.3	47	18.9	332	6.10
17	16.5			177	5.48
				75	4.72
				23	3.82

The isotherm obtained in this manner is difficult to extrapolate to pressures less than 1 mm. If, however, we plot the function P/V against P we obtain a curve which becomes a straight line of the general form $y = mx + b$ below 40 or 50 mm. Disregarding P/V values where P is less than 5 mm. (due to the hypersensitivity of the function in this region), we obtain a straight line which enables us to calculate the equilibrium pressure corresponding to any adsorbed quantity in the low pressure region. In such a manner the values obtained for the pressure given by the adsorption of 3.0 cc. per gram of catalyst were 0.36 mm. and 9.0 mm. at temperatures of 85.0 and 194.5°K., respectively. Substituting these values in the equation

$$\ln P_2/P_1 = \frac{\lambda}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

we obtain $\lambda \cong 980$ cal. This low value is in accord with the idea that this type of adsorption is caused by van der Waals forces.

For the adsorption of 0.1 cc. per gram we obtain pressures of 0.05 mm. and 77 mm. at 83.0 and 194.5°K., respectively. This leads to the following value for the heat of adsorption, $\lambda \cong 2100$ cal.

Due to such complications as capillary condensation of the adsorbate, which is easily condensable in this temperature region, the values given for the heat of adsorption should be accepted only in so far as they give the correct order of magnitude required by non-specific adsorption.

Inspection of the low temperature isotherms of MnO–Cr$_2$O$_3$ yields the following values for isobaric adsorption at 150 mm. pressure: at 85.0°K.

⁴ Stock, *Ber.*, **39**, 2066 (1906).

TABLE II

ISOTHERMS ON 40.3 GRAMS OF MnO

Temp., 83.0°K.		83.0°K.		194.5°K.	
P	V ads./m.	P	V ads./m.	P	V ads./m.
0	0.00	51	4.00	0	0.000
1	1.26	61	4.08	57	.077
2	2.48	70	4.16	79	.102
15	3.52	80	4.25	127	.154
18	3.59	91	4.34	167	.193
29	3.75	389	7.34	222	.251
36	3.83	282	6.31	295	.323
40	3.89	183	5.39	365	.380
45	3.94	15	3.57	424	.425
				493	.473
				296	.325
				141	.166

V ads./m. = 22.5; at 194.5°K. V ads./m. = 5.3. Assuming that the amount adsorbed decreases exponentially with temperature we can show that it will have decreased to less than 2.4 cc. per gram at 306°. The importance of this result will be clear after the high temperature measurements have been presented.

High Temperature Adsorption.—Attempts were made to obtain an isotherm at 218° on MnO–Cr$_2$O$_3$, for at this temperature the adsorption should be largely activated. This prediction was realized in part, for large quantities were adsorbed at speeds which were rapid but finite, the amount reaching the following high value.

V ads.	V ads./m.	P
343.5	6.70	172

However, it was impossible to obtain true equilibrium values, for after the rate had died down to a certain point it drifted steadily for weeks without any marked diminution in magnitude. The reason for this drift with carbon monoxide became apparent when a similar experiment was made at 306°. Once more the rate dropped from its initially high value to one which showed no signs of approaching zero. After five weeks' contact the adsorption reached the following value.

V_T[5]	V_{DS}	V ads.	V ads./m.	P
276.0	4.3	271.7	5.29	90

The temperature was then raised to 450° and the gas was removed from the catalyst chamber by the Sprengel pump for measurement and analysis. The results are tabulated below.

[5] These abbreviations have the following meanings: V_T = total volume of gas in the catalyst tube; V_{DS} = volume required to fill the "dead space"; V ads. = the difference of the above two, i. e., the amount adsorbed. V ads./m. = adsorption per gram of catalyst.

TABLE III

ADSORPTION OF CO ON MnO–Cr$_2$O$_3$ AT 306°

Carbon monoxide introduced, 276.0 cc.   Gas recovered by Sprengel pump, 273.4 cc.

Sample no.	CO	Analysis of recovered gas CO$_2$	%, CO$_2$
1	33.2	8.4	20.2
2	18.7	6.3	25.2
3	38.2	14.3	27.2
4	36.4	16.5	31.2
5	41.1	18.0	30.5
6	23.1	19.2	45.4
	190.7	82.7	30.3

There are two ways in which the carbon dioxide may be formed; by the reaction $2CO \longrightarrow C + CO_2$ or by actual reduction of the catalytic surface. Since the total volume of the recovered gases was practically equal to the amount of carbon monoxide originally introduced, it is evident that the former mechanism is excluded. We are, therefore, forced to the conclusion that reduction of the catalyst has taken place. It is to be observed that the proportion of carbon dioxide increases as the desorption advances.

The reduced catalyst was next reconditioned by oxidizing it in air at 300° and reducing with hydrogen at the same temperature. It was pumped off thoroughly at 450°. The influence of the time factor on reduction of the stable oxides was then studied by adsorbing a fairly large quantity of carbon monoxide at 306° and cleaning the surface with the Sprengel pump as rapidly as possible.

TABLE IV

ADSORPTION OF CO ON MnO–Cr$_2$O$_3$ AT 306°

Time of adsorption = two hours

V_T	V_{DS}	V ads.	V ads./m.	P
172.5	6.4	166.1	3.22	134

	CO	Analysis of recovered gas CO$_2$	%, CO$_2$
1. Desorption at 306°, 12 hours	115.9	0.9	0.8
2. Desorption at 450°, 8 hours	41.2	16.2	28.2
	157.1	17.1	9.8

Carbon monoxide introduced	172.5
Gas recovered	174.2

The marked rise in the yield of carbon dioxide with the rise in temperature shows that this is the main factor in the reduction of the catalyst, and that an activated adsorbate does not necessarily yield a reduced surface unless the temperature is high enough. Since the 57.3-cc. sample collected at the higher temperature did not yield as high a proportion of carbon dioxide as did the similar final portion collected after the five-week run, we

may conclude that reduction of the catalyst will take place at 306°, but only at a rate which is very small compared with the velocity of activated adsorption. Both rates are increased tremendously by raising the temperature.

On MnO an attempt was made to measure an isotherm at 444°, but the same difficulties intervened. After three weeks of contact the following values were obtained.

TABLE V

CO ON MnO AT 444°

V_T	V_{DS}	V ads.	V ads./m.	P
41.3	17.2	24.1	0.60	447

	Analysis of desorbed gas		
CO	CO_2	% CO_2	
7.9	29.1	78.6	

Carbon monoxide introduced   41.3
Gas recovered   37.0

The reduction is startlingly evident. Furthermore, the apparent decrease of 4.3 cc. in the total volume is significant, for the quantities of gas admitted normally agree with the amounts collected by the Sprengel pump within $\pm 1\%$. In this case there is a drop of some 10%, so the reaction $2CO \longrightarrow C + CO_2$ may have been proceeding simultaneously with the ordinary surface reduction by the carbon monoxide.

Rates of Adsorption.—In the investigation of the adsorption of hydrogen on these catalysts it was easy to separate the two types because adsorption of the molecular sort was relatively very small, and was negligible in the temperature range where the activated adsorption was occurring with a measurable velocity. With carbon monoxide the van der Waals forces are larger, so the molecular adsorption overlaps the activated form at all temperatures suitable for rate measurement. For this reason it was impossible to measure the activation energy required to adsorb carbon monoxide in the activated form.

General

Although the order given in this paper would indicate that the low temperature measurements were the first to be made, this was so only with the unpromoted MnO. On the mixed oxide surface all the high temperature measurements were completed before the isotherms at −78.5 and −190° were investigated. This is very important in the light of a suggestion[6] recently made which attempts to explain activated adsorption as a slow chemical reaction which removes impurities from the surface, thereby leaving a larger area available for adsorption purposes.

The experimental facts actually obtained are not in accordance with

     [6] Allmand and Chaplin, *Trans. Faraday Soc.*, **28**, 223 (1932).

such a theory, for the early attempts to obtain an isotherm at 218° led to an adsorption value of 6.70 cc. per gram of MnO–Cr₂O₃. Later, when the isotherm at −78.5° was measured it was found that the quantity adsorbed per gram at the same pressure (172 mm.) was about 5.4 cc., a marked decrease instead of a very large increase. Additional evidence against the theory has been given in Table IV, where it was shown that of 166.1 cc. of gas adsorbed in the activated form not more than 17.1 cc. could be attributed to a combination with the surface to give carbon dioxide, and that the maximum possible "molecular" adsorption would be 2.4 cc. per gram, or 127 cc. in all.

In the experiments with hydrogen reported in the earlier paper,[1] high temperature runs on both catalysts were completed before the molecular adsorption was measured, and in that case the activated adsorbate was far greater in magnitude than any of the low temperature molecular values.

In conclusion the writer wishes to thank Professor Hugh S. Taylor for his interest in the prosecution of this work, and for his part in the planning of the experimental procedure leading to the results given above.

Summary

1. The adsorption of carbon monoxide on MnO and MnO–Cr₂O₃ has been measured between −190 and +444°.

2. The adsorption takes place in two forms: a molecular form at low temperatures with zero energy of activation and a heat of adsorption of 1000–2000 calories and an activated form which becomes evident above 0°. The former is easily pumped off, the latter is very difficult to recover.

3. Unlike hydrogen, the activated carbon monoxide adsorbate causes partial reduction of the catalyst. It has been found, however, that this reduction is slow compared with the velocity of activated adsorption, and as much as 90% of the activated adsorbate has been recovered unchanged.

4. Overlapping of the two types prevented measurement of the velocity of adsorption, so it is impossible to give any values for the activation energy of the high temperature process.

5. These oxides do not catalyze the reaction $2CO \longrightarrow C + CO_2$ to any measurable extent below 300°, although evidence points to its possible occurrence on MnO at 444°.

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