[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

The Heterogeneity of Catalyst Surfaces. II. Zinc Oxide–Chromic Oxide, Manganous Oxide–Chromic Oxide, Chromic Oxide Gel

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In a previous communication[1] we have introduced a new technique to demonstrate heterogeneity of catalyst surfaces. The theory of the technique was summarized and zinc oxide was taken as an example for illustration. It seems desirable to present some additional experimental facts in support of our point of view.

Experimental

The apparatus, gases and general procedure were the same as previously reported. The catalysts examined in this investigation were manganous oxide–chromic oxide, zinc oxide-chromic oxide and chromic oxide gel. The first two will be referred to as manganous chromite and zinc chromite, respectively, as they usually are known by such names. The preparations were as follows.

Manganous Chromite.—Dissolve 45 g., of ammonium dichromate in 180 cc. of water. Add concentrated ammonium hydroxide until neutral to litmus. Add slowly with constant stirring 82 cc. of 50% manganous nitrate solution. Make up the total volume to 600 cc. with water. Wash by decantation with 1% ammonium nitrate. Filter and dry at 100–110° overnight. Heat to 400° slowly and keep at this temperature for two hours. The black product was taken as the sample. Reduction *in situ* with purified hydrogen was conducted before all measurements. This turned the preparation to a grayish green color which could very easily be oxidized to black when exposed to air.

Zinc Chromite.—Mix 0.1 *M* solutions of zinc nitrate and ammonium dichromate in the proportion of $ZnO:Cr_2O_3$ = 2:1. Add ammonium hydroxide to make it neutral to litmus. Filter and dry at 100–110° overnight. Bring the temperature up slowly to 400°. Five hours at this temperature turns the yellow precipitate to a greenish purple powder. This was weighed as the sample. Reduction *in situ* with purified hydrogen at 400° turns it to a light green. The reduced product when exposed to air undergoes a very fast, strongly exothermic reaction and becomes purple again.

Chromic Oxide Gel.—This was prepared by the "gel from jelly" method used by Turkevich, Fehrer and Taylor.[2]

Results

Manganous Chromite.—Fifty-five hundredths of a gram was taken for surface area measurement by the BET method V_m = 5.46 cc. A sample of 7.64 g. was taken for the adsorption study (V_m = 76.0 cc., surface area = 332.8 sq. m.). Hydrogen adsorptions at 1 atm. and 0.5 atm. were studied with both increasing and decreasing temperatures in steps. Adsorption on lowering the temperature was also studied at 0.25 atm. The results are given in Fig. 1. They are similar to the results obtained by Williamson.[3] It is noteworthy that there is no increase in adsorption on lowering the temperature in the range 491–273°K. at all pressures, nor was there desorption and readsorption on raising the temperature.

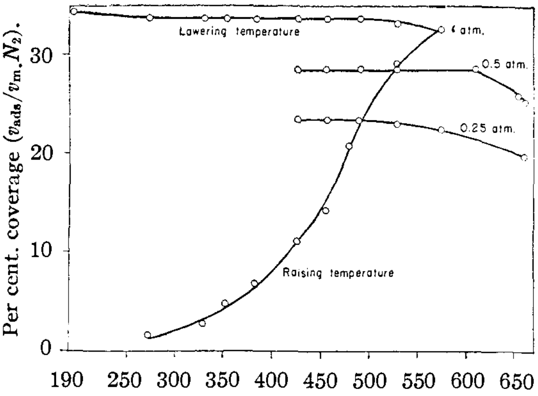

Fig. 1.—Hydrogen adsorption on manganous chromite (7.642 g. V_m = 76.00 cc.) on lowering temperature.

Zinc Chromite.—A sample of 5.967 g. was taken for study. The surface area measured with nitrogen yielded V_m = 28.24 cc. (123.8 sq. m.). Hydrogen adsorptions at 1, 0.5 and 0.25 atm. were studied. The general behavior is the same as in the case of zinc oxide. On raising the temperature, desorption and readsorption were observed. Figure 2 shows one such case.

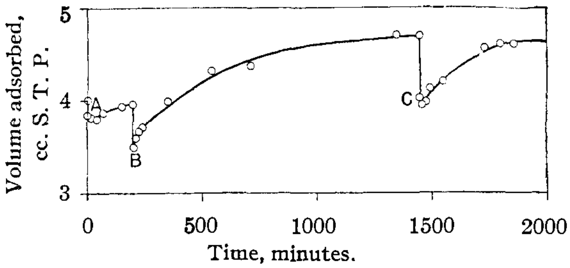

Fig. 2.—Rate of hydrogen adsorption on zinc chromite (5.967 g. V_m = 28.24 cc.) on raising temperatures: A, 329 to 353; B, 353 to 384; C, 384 to 427°K.

The surface of zinc chromite unlike that of zinc oxide is stable toward hydrogen adsorption. Not only are the adsorption values of good reproducibility, but also the surface area. Another surface area measurement made after the adsorption study was complete yielded the same value as originally. Table I gives a comparison between zinc oxide and zinc chromite.

Table II shows a set of data of hydrogen adsorption at the three pressures. The average of $V_{1/2 \text{ atm.}}/V_{1 \text{ atm.}}$ = 0.84 and $V_{1/4 \text{ atm.}}/V_{1/2 \text{ atm.}}$ = 0.80. It is noteworthy that none of the individual values deviates from the average more than the experimental error.

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[1] Taylor and Liang, THIS JOURNAL, 69, 1306 (1947).

[2] Turkevich, Fehrer and Taylor, THIS JOURNAL, 63, 1129 (1941).

[3] A. T. Williamson, Ph.D. Thesis, Princeton University, 1931.

TABLE I[a]

COMPARISON OF SURFACE AREA AND HYDROGEN ADSORPTION BETWEEN ZINC CHROMITE AND ZINC OXIDES

	Zinc chromite	Zinc oxide I[b]	Zinc oxide II	Zinc oxide III
Surface area sq. m./g.	21	25.7	15.6	5.56
% coverage at 575°K. (1 atm.)	15	6.5	8.7	14.4
% coverage at 273°K. (1 atm.) (cooled down from 575°K.)	28	9.4	19.8	45.0

[a] The samples of zinc oxide are the same as reported before.[1] [b] These values are of a different run from those reported previously.

TABLE II

HYDROGEN ADSORPTION ON ZINC CHROMITE

Temp., °K.	V.[a] cc. S. T. P. adsorbed at 1 atm.	½ atm.	¼ atm.	Ratio of adsorbed quantity[c] $\frac{V_{1/2\,\text{atm.}}}{V_{1\,\text{atm.}}}$	$\frac{V_{1/4\,\text{atm.}}}{V_{1/2\,\text{atm.}}}$
575	4.24	3.72	2.91	0.88	0.78
529	5.10	4.44	3.41	.87	.77
491	5.97	4.93	3.71	.83	.75
457	6.44	5.20	3.96	.81	.76
427	6.63	5.51	4.32	.83	.77
384	7.21	5.99	4.90	.83	.82
353	7.43	6.32	5.30	.85	.84
329	7.87	6.76	5.60	.86	.83
273	7.85	6.74	5.59	.86	.83
195	8.62	7.16	6.00	.83	.84
Ca 80[b]	14.23	11.62	9.87	.82	.85
			Average	.84	.80

[a] All the values were obtained by first getting equilibrium at 302° and then lowering successively to other temperatures. [b] 1 atm., 80.9°K.; 0.5 atm., 82.2°K.; 0.25 atm., 81.75°K. [c] Experimental uncertainty in these two columns is 5%.

A "pump-off at temperature" technique has been studied since this has been used as one of many ways to differentiate chemisorption from physical adsorption. Ten hours were usually allowed for evacuation. This was applied at temperatures of the liquid air bath, 195, 273 and 329°K. The results showed that the gas adsorbed below 195° can be pumped off at all temperatures below or at this temperature but the quantity *adsorbed at* 195°K. could not be pumped off at this temperature. When pumping at 273°K., all the gas adsorbed at or below 353°K. was removed and at 329°K. gas adsorbed at 384°K. could be pumped off also.

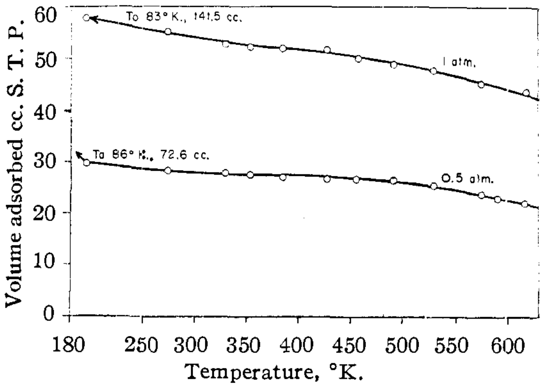

Fig. 3.—Hydrogen adsorption on chromic oxide gel (4.857 g., V_m = 210 cc.) on lowering temperature.

Chromic Oxide Gel.—A 6.376-g. sample dried at 300° was taken for study. It was kept at 350° overnight to remove any residual water. Unexpectedly a loss of 1.519 g. in weight was found and 4.857 g. was therefore taken as the sample weight. When heated to 400° large amounts of gases were released, but no water was observed. On keeping the sample at this temperature, sixty-six hours of continuous evacuation were required to build up the first vacuum. However, during the adsorption measurements, ten hours, the standard length of time for evacuation in this Laboratory, gave a good vacuum. The final apparent volume of the sample shrank to about one-half. As this final sample underwent reaction when exposed to air, it was not weighed again.

Despite this vigorous treatment, the surface area measurements gave V_m = 210 cc. S.T.P. (921 sq. m. or 189.5 sq. m./g.). This large specific surface area is doubtless responsible for the adsorption of measurable amounts of helium at liquid air temperatures as reported by Howard and Taylor.[4] The quantity of adsorbed helium found by us at 81°K. and 1 atm. was 0.7 cc. or 0.3% coverage. Hydrogen adsorption was studied at 1 and ½ atm. over the temperature range 81–600°K. Adsorption isobars are given in Fig. 3. The general shape is reversed sigmoid.

Discussion

In our earlier communication we pointed out that a horizontal region in the adsorption isobar on lowering the temperature would constitute evidence that no desorption from the catalyst surface had occurred as one passed from lower to higher temperatures in studying the adsorption of the gas. The data for manganous chromite, shown in Fig. 1, are an example of such behavior. The horizontal part does not necessarily indicate uniformity of the adsorbing surface. It may only mean that the activation energy of desorption is too high to permit measurable desorption, at the working pressure, as the temperature is raised from 273 to 491°K. This, in its turn, suggests that, in this same temperature range, adsorption occurs, starting with a clean surface, on the same areas for the same volumes of gas adsorbed at the several temperatures. This is exactly the condition necessary to permit the valid calculation of the activation energies of adsorption from data on the rates of adsorption. The data of Taylor and Williamson[5] on manganese–chromium oxide in the temperature range 373–405°K. are thus validated. It is, therefore, of interest to recall that these measurements indicated an activation energy,

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[4] Howard and Taylor, THIS JOURNAL, 56, 2259 (1934).

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

$E = 5.9$ kcal. per mole for the first 10 cc. adsorbed, $E = 9.5$ kcal. per mole for the next 5 cc., and $E = 10.4$ kcal. per mole each for adsorption from 15 to 20 and 20 to 25 cc. adsorbed. It is evident that the adsorption area from 15 to 25 cc. is substantially uniform, that from 10 to 15 cc. approximately the same. The activation energy for the first 10 cc. is, however, conspicuously lower. The marked divergence of the activation energy in this area is indicative of a partial heterogeneity of the surface.

The cases of zinc chromite and chromium oxide gel conform in all details to the case of zinc oxide previously reported. They show the reversed sigmoidal chemisorption isobars as one makes measurements at a given pressure proceeding from high to low temperature. They provide additional examples of desorption, followed by readsorption, outside the range of measurable van der Waals adsorption, as one changes from lower to higher temperature at a given pressure. They serve therefore to generalize the results first exemplified with zinc oxide as to heterogeneity of surfaces.

The data obtained by the "pump off at temperature" technique in the case of zinc chromite indicate definitely that this is not a good criterion for distinguishing between van der Waals and chemisorption. The gas adsorbed at or below 353°K. can be removed by pumping at 273°K. Much of this is chemisorbed hydrogen. This is even more true of the gas adsorbed at 384° and removable by pumping at 329°K. On the other hand, the gas adsorbed below 195°K., in part van der Waals, in part chemisorbed, can be removed at 195°K., while that adsorbed at 195°K. could not be pumped off at temperature. It is evident that removal of gas by evacuation is not governed solely either by chemisorption or van der Waals adsorption but depends in the chemisorption case on the relative magnitudes of the energy of activation of desorption $(E + \lambda)$ and of RT in the expression for the velocity of desorption $v_d = ke^{-(E + \lambda)/RT}$.

The data of Table II point to the occurrence of chemisorption on zinc chromite even at 80°K. where it has been customary to think of the adsorption as essentially due to van der Waals forces. Physical adsorption of hydrogen at 80°K., which is well above the critical temperature of hydrogen, should bear a more nearly linear relation to the pressure than is indicated by the adsorption ratios $v_{1/2\ \text{atm.}}/v_{1\ \text{atm.}} \approx v_{1/4\ \text{atm.}}/v_{1/2\ \text{atm.}} \approx 0.8$. Even the extra amounts of gas adsorbed as one lowers the temperature from 195 to 80°K. conform to this ratio of 0.8 (see Table II). Much of this gas may be chemisorbed gas, necessarily with a low energy of activation, as the measurements of Taylor and Strother[6] would suggest. With chromic oxide gel the adsorptions at 80°K. are more nearly linear with the pressure. All the evidence points to a much larger proportion of van der Waals adsorption of hydrogen at 80°K. than chemisorption in the case of chromic oxide gel although the slow reaction of hydrogen and deuterium[7] and the heats of adsorption studied by Beebe and his co-workers[8] indicate some chemisorption even at liquid air temperatures.

To justify the argument for the establishment of heterogeneity of surfaces, we must again point out that the gas desorbed as shown in Fig. 2 is chemisorbed gas. The physical adsorption of nitrogen on zinc oxide has been shown to be immeasurably small at 329°K. Since the critical temperatures of hydrogen and nitrogen are 33.4 and 126°K., respectively, and $126/33.4 = 3.78$, it will be safe to say that the physical adsorption of hydrogen is negligible above 273°K. on surfaces of the areas here considered. The non-specificity of physical adsorption permits us to apply the same reasoning to zinc chromite with the same order of magnitude of surface area. This can be further justified by the fact that the heats of hydrogen adsorption at liquid air temperatures on chromic oxide gel are not abnormally high,[8] and that the zinc chromite we have is actually a mixture of zinc oxide and chromic oxide. Accordingly, the case of Garner and Kingman[9] cited in the previous communication actually involves chemisorption and therefore conforms to the ideas herein discussed.

Summary

Zinc oxide–chromium oxide catalysts and chromium oxide gel reveal heterogeneity of surface by techniques of measuring chemisorption with increasing and decreasing temperatures at constant pressure, as previously noted in the case of zinc oxide.

Manganous oxide–chromium oxide catalysts do not show desorption–readsorption phenomena on raising the temperature. The isobar on decreasing temperature is consequently horizontal over a considerable temperature range. The surface nevertheless shows a partial heterogeneity.

The criterion of "pumping-off at temperature" is doubtful in distinguishing van der Waals and chemisorption of hydrogen in certain temperature ranges with these catalysts.

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[6] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

[7] Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

[8] Beebe and Orfield, THIS JOURNAL, **59**, 1627 (1937); Beebe and Dowden, *ibid.*, **60**, 2912 (1938).

[9] Garner and Kingman, *Nature*, **126**, 352 (1930).