has been shown to be false; the yield of methyl ethyl ketone, however, is poor and the bisulfite method is to be preferred.

Summary

1. The vapor pressures, densities and refractive indices for pure methyl ethyl ketone, purified by two methods, have been determined as functions of the temperature.

2. The heat of vaporization and the molal entropy of vaporization have been calculated.

3. The solid addition compound of the ketone and sodium iodide dihydrate has been investigated.

AUSTIN, TEXAS RECEIVED JULY 16, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Activated Adsorption of Hydrocarbons

BY JOHN TURKEVICH AND HUGH S. TAYLOR

We have studied the adsorption of ethylene as a typical unsaturated hydrocarbon and methane, ethane and propane as saturated hydrocarbons on typical hydrogenating catalysts. As oxide catalyst we have used the manganese chromite catalyst examined by Taylor and Williamson,[1] for hydrogen and carbon monoxide adsorption. Reduced copper was chosen as a typical metallic catalyst.

Experimental

Apparatus.—The apparatus was of the type used at Princeton for the study of gas adsorption on catalysts.[1] It consisted of a gas-purifying train, a gas buret compensated for variation in atmospheric temperature and pressure, a catalyst tube, a mercury manometer and a pumping system, a mercury diffusion pump backed by an oil pump. Gases desorbed from the catalysts by the mercury vapor pump could also be collected by an automatic Sprengel pump[2] and fed into a Bone and Wheeler gas analysis apparatus.[3] The entire system was made of Pyrex glass except for the soft glass burets, which were attached by ground-glass joints cemented with picene. The gas buret could be read with an accuracy of 0.1 cc. and the pressure reading to 1 mm.. The gas analyses were accurate to 1%.

Preparation of Materials

Manganese Oxide–Chromium Oxide Catalyst.—172 g. of C. P. ammonium chromate was dissolved to make two liters of solution; 234 g. of C. P. manganous nitrate (a 50% solution) was dissolved to make two liters of solution. These two solutions were mixed, allowed to stand for eighteen hours and the supernatant brownish liquor decanted. The precipitate was washed with two liters of 0.2% ammonium nitrate solution and filtered. The residue was suspended in four liters of 0.2% ammonium nitrate solution, decanted and repeatedly washed with 10% ammonium nitrate solution. The suspension was filtered again and dried overnight at 110°. The dry mass was heated gradually to 400° in a muffle furnace and kept there for two hours. The catalyst was reduced *in situ* by hydrogen at 450°. The reduction was considered complete when a tared phosphorus pentoxide tube attached to the exit tube of the catalyst showed no increase in weight after two hours.[4]

Copper Catalyst.—One hundred grams of Kahlbaum copper oxide for organic combustions was slowly reduced *in situ* below 200° by means of hydrogen gas. A long induction period was followed by a fast reduction at about 160°. The temperature was lowered to 120° while the reduction proceeded. The final reduction was made at 200°. Passage of hydrogen was continued until there was no increase during two hours in the weight of a tared phosphorus pentoxide tube attached to the exit tube of the catalyst chamber. The copper catalyst was pumped off for fifty hours at 400° with a mercury diffusion pump and an oil pump.

Gases.—Helium was obtained by passing tank helium through a trap containing activated carbon and immersed in liquid air. The carbon had been evacuated overnight at 500°. Hydrogen prepared electrolytically was passed through a furnace containing platinized asbestos and then dried over calcium chloride and phosphorus pentoxide. Nitrogen from cylinders was passed over metallic copper shavings heated to 500° and dried over phosphorus pentoxide. Ethylene was obtained from cylinders, condensed in a liquid air trap and the middle fraction used. Ethane, analyzing $C_{1.87}H_{5.74}$, from cylinders, was in part used. For adsorption isotherms, ethane was prepared from hydrogen and ethylene by catalytic reaction over copper. Methane was synthesized from carbon monoxide and hydrogen over nickel, the residual reactants being removed by burning over copper oxide at 350°. The propane was obtained by fractionation of a cylinder product and analyzed $C_{3.2}H_{8.4}$.

Temperature Control.—Vapor baths were used above 0°. Liquid air, solid carbon dioxide and ether, and ice were used for the low temperature work, an oxygen thermometer recording the exact temperature with liquid air.

Procedure

The dead space in the catalyst tube was determined by the measurement of the volume of helium added and the pressure of the gas produced in the catalyst tube. The method of calculation was that explained by Williamson.[4] The validity of the assumption that no helium was adsorbed, was tested by measuring the helium isotherms at

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

(2) Dunoyer "Vacuum Practice," G. Bell and Sons, London, 1926.

(3) Bone and Wheeler, *J. Soc. Chem. Ind.*, **28**, 10 (1908).

(4) Williamson, Thesis, Princeton University, 1931.

more than two temperatures and showing that they all gave the same variant and invariant dead spaces.

The van der Waals isotherms were obtained by adding known volumes of gas to the catalyst and observing the pressure produced. Equilibrium was established very quickly. In studying desorption, known amounts of the gas were pumped off by a Sprengel pump and the points on the isotherm were approached from the high pressure side. Coincidence of the two isotherms—one obtained with increasing pressure, the other with decreasing pressure—was taken as the criterion of equilibrium.

In the temperature regions where the rate of change of pressure of the gas in the catalyst chamber was appreciable, rate studies were made. The rate studies when decomposition and desorption take place have only qualitative significance. After indicated intervals the gases were pumped from the catalyst by a mercury vapor pump, transferred to the Bone and Wheeler gas analysis apparatus by means of the Sprengel pump and analyzed in the following way: carbon dioxide was determined by absorption in concentrated sodium hydroxide; unsaturated hydrocarbons were determined by absorption in fuming sulfuric acid followed by absorption in sodium hydroxide; oxygen was absorbed by alkaline pyrogallol; hydrogen was determined from the loss in volume after passage over copper oxide heated to 250°. Two slow passages were sufficient to remove all the hydrogen. Saturated hydrocarbons were analyzed by combustion over copper oxide at 550° and the determination of the amount of carbon dioxide produced.

A large number of preliminary experiments were first made on a number of catalyst preparations of manganese–chromium oxide in order to define the best order of conduct of the experiments. This ascertained, a series of experiments was devised which are presented in outline in the following Table of Experimental Results, and de-

TABLE OF EXPERIMENTAL RESULTS

Expt.	Catalyst	Vol. of gas introduced, cc. N. T. P.	T, °C.	Time of contact, hrs.	Vol. of exit gas, cc. N. T. P.	Analysis in %			
						CO_2	C_nH_{2n}	H_2	Satd. hydrocarbon of formula
1	$MnO-Cr_2O_3$I	39.8 C_2H_4	0	24	39.8	0	100	0	0
2	I	34.0 C_2H_4	110	12	34.0	0	100	0	0
3	I	18.0 C_2H_4	184	24	10.9	0	31	0	68 $C_{1.58}H_{5.16}$
			302	12	2.0	2	14	41	43 CH_4
			350	12	18.8				
			444	16	12.0	9	2	59	30 CH_4
4	I	30.0 C_2H_4	302	72	28.0	2	37	13	48 $C_{1.38}H_{4.76}$
			444	12	33.1	5	0	84	11 $C_{1.17}H_{4.34}$
5	I	17.2 C_2H_4	444	24	29.3	4	10	34	51 CH_4
6	I	15.3 C_2H_4	444	24	22.7	5	10	25	64 CH_4
7	I	19.3 C_2H_4	184	72	14.1	0	0	52	48 C_2H_6
			444	24	19.3	12	0	45	43 CH_4
8	II	32.6 H_2	184	18	..	..	...	..	...
		15.9 C_2H_4	184	12	15.9	0	27	2	72 $C_{1.74}H_{5.68}$
			302	12	0	..	...	..	...
			444	12	26.2	3	0	89	8 $C_{1.53}H_{5.06}$
9	II	50.8 H_2	302	9	..	..	...	..	...
		17.8 C_2H_4	302	14	23.8	0	1	51	47 $C_{1.73}H_{5.46}$
			444	12	28.2	2	0	82	16 $C_{1.13}H_{4.26}$
10	II	5.1 C_2H_4 5.6 H_2	302	16	3.0	..	...	..	...
11	II	9.0 C_2H_4	444	12	9.9	9	2	14	74 $C_{1.16}H_{4.32}$
		11.0 H_2	444	24	25.0	6	1	44	47 CH_4
12	II	8.0 C_2H_4 9.9 H_2	444	24	23.0	4	2	51	42 CH_4
13	III	77.4 C_2H_6	0	24	77.4	0	0	0	100 C_2H_6
14	III	59.7 C_2H_6	184	24	59.7	0	0	0	100 C_2H_6
15	III	13.7 $C_{1.87}H_{5.74}$	302	24	12.2	0	0	0	100 $C_{1.87}H_{5.74}$
16	III	10.8 $C_{1.87}H_{5.74}$	444	24	23.0	7	0	31	62 CH_4
17	III	18.3 CH_4	0	12	18.3	0	0	0	100 CH_4
18	III	23.3 CH_4	184	12	23.3	0	0	0	100 CH_4
19	III	20.1 CH_4	302	12	20.1	0	0	0	100 CH_4
20	III	17.8 CH_4	444	120	25.7	10	0	20	70 CH_4
21	III	73.1 C_3H_8	110	12	73.1	0	0	0	100 C_3H_8
22	III	11.7 C_3H_8	302	24	9.4	0	0	0	100 $C_{2.64}H_{7.28}$
23	III	4.8 C_3H_8	444	3	9.8	0	0	13	87 $C_{1.18}H_{4.36}$
24	Copper	62.9 C_2H_4	−78.5	24	62.9	0	100	0	0
25	Copper	78.0 C_2H_4	0	168	71	0	70	0	30 C_2H_6
26	Copper	81.0 C_2H_4	−78.5	24	81.0	0	100	0	0
27	Copper	44.1 C_2H_4	56.0	24	44.1	0	87	0	13 C_2H_6

REMARKS TO TABLE

The table gives representative examples of the experiments performed. The numbering of the experiments is the order of performance. The same numbering is used in the table, the discussion below and the figures.

1. The adsorption of ethylene was rapid and reproducible. The desorption isotherm coincides with the adsorption isotherm; *cf.* Fig. 1.

2. The adsorption of ethylene was rapid. The adsorption curves could be reproduced but they did not coincide with the desorption isotherms. The latter showed greater adsorption at corresponding pressures; *cf.* Fig. 1.

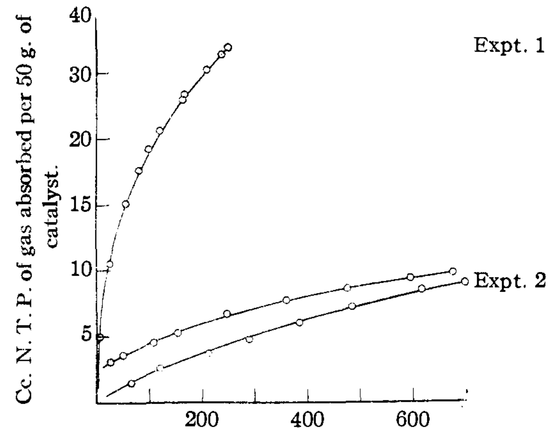

Fig. 1.—Absorption isotherms of ethylene on MnO–Cr_2O_3 at 0 and 10°.

3. The adsorption of ethylene was not reproducible. At this temperature of 184° there was a steady decrease of pressure with time.

4. The pressure decreased the first five minutes and then increased.

5–6. Pressure of system increased steadily.

7. The catalyst surface was covered by carbon due to previous decomposition of ethylene at higher temperatures. This experiment was performed to study the effect of carbon deposition on the adsorption and decomposition of ethylene; *cf.* Expt. 3.

8. The surface was allowed to adsorb hydrogen until the pressure of hydrogen reached a steady value. The behavior of ethylene was then studied on such a surface. The decrease of pressure of ethylene was faster on such a surface than on either a clean surface or on one covered by carbon; *cf.* Expts. 3 and 7.

9–10. The pressure of the system decreased.

11-12. The pressure of the system increased.

13. The adsorption was rapid and reversible; *cf.* Fig. 2.

14. No adsorption.

15. Pressure decreased steadily.

16. The pressure decreased during the first ten minutes and then increased steadily.

17. Adsorption was rapid and reversible; *cf.* Fig. 2.

18-19. No adsorption or decomposition.

20. Very slow decrease in pressure.

21. Adsorption was rapid and reversible; *cf.* Fig. 2.

22. The pressure decreased steadily.

23. The pressure decreased for the first two minutes and then increased.

24. The adsorption was rapid and reversible.

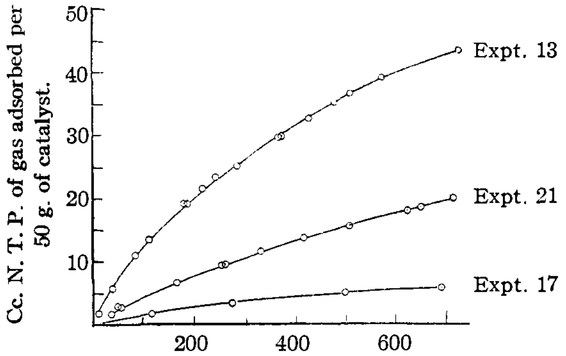

Fig. 2.—Adsorption isotherms of methane, ethane and propane on MnO–Cr_2O_3.

25. A series of adsorption and desorption isotherms were determined at 0°. The adsorption isotherms were reproducible, but the desorption curves always showed greater adsorption at corresponding gas pressures.

26. The copper surfaces used here contained appreciable quantities of adsorbed ethylene put on the surface in the previous experiments at 0°. The adsorption process was reproducible and reversible. The lower capacity of the surface for van der Waals adsorption compared with a clean surface of Expt. 24 should be noted; *cf.* Fig. 3.

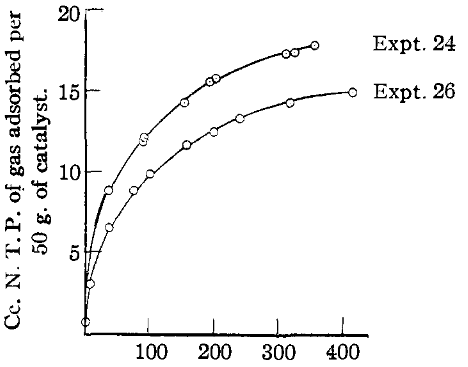

Fig. 3.—Adsorption isotherms of ethylene on copper.

27. The adsorption process was slow and not reproducible.

28–32. Numerous experiments with ethylene on copper at the temperatures 184, 219, 302, 354 and 444° all showed a decrease of pressure with time. The rate curves were not reproducible, but showed a slowing up of the adsorption process on successive experiments at a given temperature. The gases obtained on pumping were invariably ethane and ethylene. No hydrogen or methane could be desorbed from the surface in the above temperature range. Analysis of the gases showed that considerable carbon was left on the copper surface.

signed to exhibit the progressive change in the nature of the association of ethylene with the oxide surface as the operating temperature was increased.

Discussion

There is, in all of the experimental data presented, a certain uniformity of results. In a low temperature range, determined by both gas and surface, there is a rapid, reversible adsorption which may be ascribed to an adsorption of the gas molecules by van der Waals forces. In an intermediate range, also characteristic for a given gas and surface, there is an adsorption which is measurable in speed and which shows hysteresis effects on desorption from surfaces already more or less saturated at higher pressures. The operation of the time factor is an index that the adsorption involves an activation energy. At some of the temperatures employed, gases so adsorbed may be recovered unchanged on evacuation. At still higher temperatures, the process of activated adsorption occurs with increasing velocity, but, in the case of the complex gases here studied, there intrude processes of decomposition and interaction of fragments which are revealed in the subsequent desorption process by differences in the nature of the desorbed gas from that adsorbed. The changes occurring are characteristic of the surface under study.

For example, with manganese oxide–chromium oxide, it is evident that at or below 0° the adsorption of ethylene is of the van der Waals type. At 110° there is, in addition to van der Waals adsorption, some activated adsorption with negligible decomposition. At 184° activated adsorption is accompanied by decomposition of the ethylene. The rate of adsorption is, however, faster than the rate of desorption of decomposition products. The presence of ethane in the gas phase even without added hydrogen shows that ethylene both undergoes decomposition and is actually hydrogenated at 184°. With hydrogen present specificity in catalytic activity, of which Lazier and Vaughen write[5] in contrasting metal and oxide catalysts for hydrogenation of olefins, is, therefore, only one of degree. All the ethylene adsorbed at 184° cannot be desorbed at this temperature but is recovered as other gases at higher temperatures.

At 302° the time variation of the pressure of the gases shows in a striking manner the relative rates of the different processes that take place. During the first five minutes the rapid pressure decrease shows that activated adsorption is the predominant phenomenon. Afterward, the slow pressure increase shows that the velocities of decomposition and desorption are of the same order of magnitude as the rate of activated adsorption. Ethylene can still be recovered from the surface at this temperature but, in contrast to behavior at 184°, hydrogen is now found in the gas phase. Appearance of carbon dioxide in the desorbed gas shows that at 302° a reduction of the catalyst is also occurring.

At 444°, when ethylene is admitted to the catalyst, the pressure steadily increases. The decomposition–desorption processes are now the most rapid. No net hydrogenation occurs, since ethane is decomposed on the catalyst at this temperature. Decomposition of ethylene to methane, carbon and hydrogen, and reduction of the catalyst are the important reactions at this temperature.

The deposition of carbon in the catalyst mass decreases the rate of activated adsorption and minimizes the decomposition of ethylene. It does not inhibit appreciably the hydrogenation of ethylene in spite of the fact that hydrogen adsorption is decreased, as shown by the considerable amount of hydrogen in the gas phase (Expt. 7). Activated adsorption of hydrogen favors the activated adsorption of ethylene. Both the rate of adsorption and its subsequent reaction are increased on manganese oxide–chromium oxide surfaces containing hydrogen. At 302° activated adsorption of hydrogen decreased the amount of carbon dioxide formation, repressed the decomposition of ethylene to yield methane and correspondingly increased the ethane yield.

The saturated hydrocarbons methane, ethane and propane are qualitatively similar in their behavior on manganese oxide–chromium oxide. They all show van der Waals adsorption at 0°. Activated adsorption is not indicated below 302° and then only with ethane and propane and accompanied by some decomposition. At higher temperatures decomposition is more rapid and the desorption products are hydrogen and methane.

With the copper catalyst activated adsorption of ethylene occurs at a much lower temperature than with the oxide catalyst studied. At −78° our results show that the adsorption is reversible and of the van der Waals type. At 0° some activated adsorption is occurring. The excess

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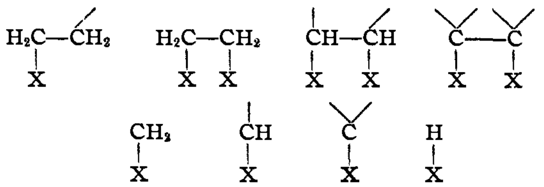
(5) Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

hydrogen used in the preparation of the catalyst, and not removable by evacuation of the catalyst at high temperatures without sintering of the catalyst, reacts with ethylene adsorbed at 0°. In addition to this reaction, however, there is an adsorption not completely reversible on desorption at this temperature. The discrepancy between adsorption and desorption data increases with increasing time of contact with the copper. Ethane is always obtained in the desorbed gases even after ten successive experiments, indicating that some of the adsorbed gas must have undergone processes both of dehydrogenation and hydrogenation. Such activated adsorption of ethylene at 0° decreased the capacity of the surface to adsorb ethylene by van der Waals forces at −78°. Howard[6] found a similar behavior with chromium oxide gel in his study of the effect of activated adsorption of hydrogen or the van der Waals adsorption of the gas.

At temperatures above 0° the rate of activated adsorption of ethylene increases and becomes measurable. The actual rate curves are not reproducible, however, due to a cumulative poisoning of the surface by accompanying decomposition reactions. The gases desorbed are essentially ethane and ethylene and it is to be emphasized that hydrogen and methane do not appear in measurable amounts. This divergence from the behavior of the oxide surface is noteworthy.

We consider that the experimental evidence that has been given in the preceding suggests that the activated adsorption of ethylene on a catalyst surface involves the formation of homopolar bonds between the surface atoms and either the carbon or the hydrogen atoms. If the latter occur, the carbon–hydrogen bond in ethylene must be broken, for hydrogen has only one electron available for bond formation. The formation of a carbon–catalyst bond may produce a variety of changes in what was originally an ethylene gas molecule. The data suggest that on the surface of the catalyst (X) after activated adsorption of ethylene some of the following fragments may be present.



The relative distribution of the fragments will depend on catalyst and temperature conditions. It is easy to see how, with such stages of resolution of the ethylene molecule on the surface, the various decomposition, polymerization and hydrogenation products might arise. Such a concept of the catalyst–reactant association is in best accord with our present concept of mechanism in the catalyzed ammonia decomposition and synthesis.[7] This latter case is, however, so very much simpler because of the gaseous nature of both end-products, N_2 and H_2, and of the smaller number of nitrogen–hydrogen compounds that can result from the N, H, NH and NH_2 fragments.

It is evident also that such a concept of the surface complexes is in best accord with recent observations that, in the interaction of deuterium with ethylene,[8] not only does addition to form the saturated compound occur, but that, under certain experimental conditions, an exchange reaction $C_2H_4 + D_2 = C_2H_3D + HD$ occurs. It was shown that this exchange did not involve a hydrogenation–dehydrogenation reaction, since ethane and deuterium did not exchange on the surface under conditions in which the process occurred with ethylene and deuterium. Our experiments at once suggest the explanation for the non-occurrence of exchange with the ethane, since our adsorption measurements show that ethane only undergoes activated adsorption on the surfaces studied at much higher temperatures than ethylene. Our adsorption evidence, however, compels the conclusion that in the upper ranges of temperature studied by us an exchange between deuterium and ethane must occur readily. We are investigating a number of such exchange reactions between saturated adsorbed molecules and deuterium at various surfaces.

Summary

Adsorption characteristics and decomposition products of ethylene, ethane, methane and propane on manganese oxide–chromium oxide were determined in the temperature range of −78.5 to 444°.

Adsorption characteristics and decomposition products of ethylene on active copper were determined in the temperature range of −78.5 to 444°.

The behavior of ethylene on manganese oxide–

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(6) Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

(7) See, for example, Frankenburger, *Z. Elektrochem.*, **39**, 45, 97, 269 (1933).

(8) Farkas, *J. Soc. Chem. Ind.*, **53**, 491 (1934).

chromium oxide and on active copper was interpreted in terms of activated adsorption and ethylene decomposition.

The experimental observations lead to a concept of the surface-gas system in accord with our knowledge of various catalytic reactions on such surfaces. The conditions for exchange reactions between deuterium and ethylene or ethane are also defined by the adsorption measurements.

PRINCETON, NEW JERSEY RECEIVED JULY 17, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Adsorption of Gases by Chromium Oxide Gel

BY JOHN HOWARD[1] AND HUGH S. TAYLOR

In a paper describing measurements of the heats of adsorption of hydrogen and carbon monoxide on zinc oxide, chromium oxide and mixtures of the two, Garner and Kingman[2] state, *inter alia*, that the adsorption of hydrogen on chromium oxide is too small to measure. Some data of Sherman reported in outline by Taylor[3] show, however, that chromium oxide, prepared by the methods of Lazier and Vaughen,[4] is an excellent catalyst for the reconversion of parahydrogen to the ortho form, suggesting, therefore, that appreciable activated adsorption of hydrogen must occur. Lazier and Vaughen show that chromium oxide, suitably prepared, is an excellent catalyst even for the hydrogenation of ethylene, in contrast to the behavior of other hydrogenating oxide catalysts. In view of these facts it seems desirable to investigate the adsorptive properties of chromium oxide of the type found "most convenient and reliable" by Lazier and Vaughen, special attention being paid, accordingly, to the preservation of the catalyst in the unglowed condition. There is already definite evidence in the literature[5,6,7,8] that adsorptive capacity for gases and in solution, and also the chemical and catalytic reactivity of chromium oxide, are very sensitive to this exothermic change from an amorphous to a crystalline state as revealed by Debye-Scherrer x-ray patterns.[4] The adsorption measurements of Schmidt[8] with a variety of gases indicate that he may have been using a glowed sample, with which Taylor and Sherman found negligible activity in the para hydrogen reconversion process. It was hoped also that such measurements might yield some reasons for the excellent behavior of chromium oxide as a catalyst for hydrogenation of ethylene in contrast to the behavior of, for example, manganese oxide-chromium oxide, the adsorption characteristics of which have been studied by Turkevich and Taylor.[9]

Experimental

Apparatus.—The adsorption measurements were carried out in the standard Princeton method.[10] The adsorbed gases could be recovered quantitatively with an automatic Sprengel pump[11] and could be analyzed in a Bone and Wheeler apparatus.[12]

Adsorbent.—The method of preparation of Lazier and Vaughen[4] was followed using 0.04 molar solutions of chromium nitrate to which was added, in the cold, with violent stirring, an equivalent quantity of 0.1 normal ammonium hydroxide. After washing by decantation, using a mechanical stirrer, for several days, until peptization began to occur, the precipitate was filtered and the voluminous gel so obtained was dried at temperatures gradually increasing to 200°. The drying was completed in a stream of purified hydrogen for twenty-four hours at 375°, *in situ*, in the tube used for the adsorption measurements. Five samples, from three different batches, prepared in an identical manner, were used: Cr_2O_3 I, 45 g. from batch 1; Cr_2O_3 II, 33 g., and Cr_2O_3 III, 38 g., both from batch 2; Cr_2O_3 IV, 5 g., and Cr_2O_3 V, 12 g. from batch 3.

Gases.—Helium was obtained by passing tank helium through a trap containing activated carbon and immersed in liquid air. The carbon had been evacuated overnight at 500°. Hydrogen prepared electrolytically was passed through a furnace containing platinized asbestos and then dried over calcium chloride and phosphorus pentoxide. Nitrogen from cylinders was passed over metallic copper shavings heated to 500° and dried over phosphorus pentoxide. Ethylene was obtained from cylinders, condensed in a liquid air trap and the middle fraction was used. Ethane from cylinders was dried over phosphorus pentoxide. A pronounced hysteresis in the adsorption of this gas at −78° indicates that the gas was not pure but a mixture of

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(1) Commonwealth Fellow, Princeton University, 1931-1933.

(2) Garner and Kingman, *Trans. Faraday Soc.*, **27**, 322 (1931).

(3) Taylor, *Nature*, **128**, 636 (1931).

(4) Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

(5) Wohler, *Kolloid Z.*, **38**, 97 (1926).

(6) Budnikoff and Krause, *ibid.*, **55**, 330 (1931).

(7) Nikitin, *Z. anorg. angew. Chem.*, **155**, 358 (1926).

(8) Schmidt, *Z. physik. Chem.*, **133**, 263 (1928).

(9) Turkevich and Taylor, THIS JOURNAL, **56**, 2254 (1934).

(10) *Cf.* (a) Taylor and Williamson, *ibid.*, **53**. 2168 (1931); (b) Taylor and Sickman, *ibid.*, **54**, 602 (1932).

(11) Dunoyer-Smith, "Vacuum Practice," G. Bell & Sons, London, England, 1926.

(12) Bone and Wheeler, *J. Soc. Chem. Ind.*, **28**, 10 (1908).