the basic nitrites,[8] the cobalticyanides[9] and the ferricyanides.[10] The bromate method is the standard one for the fractionation of the yttrium earths, but is not particularly effective for the preparation of pure yttrium. The new method compares favorably in efficiency with the nitrate fusion, chromate and basic nitrite methods. It appears to be superior to the ferricyanide and cobalticyanide methods. Grant and James[10] report a very high efficiency for the ferricyanide method, but no supporting data have been published.

Summary

A new method for the separation of yttrium from the yttrium earths has been proposed, and has been found to compare favorably in efficiency with the methods now in use.

DURHAM, NEW HAMPSHIRE RECEIVED MAY 1, 1936

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[8] H. C. Holden and C. James, THIS JOURNAL, **36**, 1418 (1914).

[9] J. P. Bonardi and C. James, *ibid.*, **37**, 2642 (1915).

[10] A. J. Grant and C. James, *ibid.*, **39**, 933 (1917).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activated Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide. The Effect of Water Vapor

BY ROBERT L. BURWELL, JR., AND HUGH S. TAYLOR

Poisons such as water vapor have been presumed to effect the retardation of catalytic processes by being adsorbed on the "active spots," thus blocking access of the reactants to such catalytically effective sections of the surface.[1] This access of reactants to catalytically effective sections of the surface consists according to Taylor[2] of an activated adsorption of the reactants on such regions of the surface. Reversible poisoning would accordingly result from an activated adsorption of the poison on the active sections of the surface, an adsorption possessed of energy relations such that the activation energy of desorption would be large compared with that of the other components of the system. In this fashion the activated adsorption of the reactants may be hindered.

Taylor and Sickman[3] and Taylor and Strother[4] investigated the activated adsorption of hydrogen on zinc oxide. The former investigators further reported that water vapor exerted an inhibitory influence on a catalytic action which they studied, the decomposition of propanol-2 on zinc oxide. It thus appeared of interest to study the effects of water vapor on the activated adsorption of hydrogen on zinc oxide.

Experimental

Rates of the activated adsorption of hydrogen on zinc oxide were determined by means of an apparatus and method similar to that described by Taylor and Strother.[4] The purified hydrogen could be saturated with water vapor at any desired temperature between 0° and room temperature by diverting it through a spiral bubbling column filled with distilled water and maintained at the desired temperature. Carbon monoxide was prepared by dropping formic acid on hot sulfuric acid. It was purified by passage over copper heated to 450°, soda lime, calcium chloride and phosphorus pentoxide. To supply water vapor to the adsorbent preliminary to rate runs, the apparatus was further provided with a buret of 410-cc. capacity. The zinc oxide was prepared from zinc oxalate as described by the above authors.

All gas volumes reported have been corrected to N. T. P. All the experiments described in this paper were performed on two samples of the same batch of zinc oxide. These samples were 3B, weight 16.5 g., and 3C, weight 22.7 g.

Before the start of these researches these adsorbents had been subjected to a series of determinations of the rates of activated adsorption, first of carbon monoxide and then of hydrogen. During the course of these adsorption measurements the activity of the surface had fallen slowly but steadily.

Results and Discussion

After a number of runs with hydrogen at 184 to 302°, it was observed that, at the completion of the adsorption, the preparations, notably 3B, had

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[1] See, for example, Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **A97**, 262 (1920); Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131 (1929).

[2] Taylor, THIS JOURNAL, **53**, 578 (1931).

[3] Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[4] Taylor and Strother, *ibid.*, **56**, 586 (1934).

a distinctly grayish appearance. On evacuation at 400° the original color of the preparation reappeared. A dark gray condensate gradually appeared above the furnace level on the walls of the capillary tube leading from the catalyst bulb.

It appears that, by reduction, there is formed a certain quantity of metallic zinc which subsequently distils from the catalyst bulb during evacuation. Only a small portion of the adsorbed hydrogen reduces the zinc oxide. Thus in 32 runs on preparation 3C, over 334 cc. of hydrogen was adsorbed. One gram of zinc would have been formed if all of this had led to reduction; actually less than 0.05 g. appeared. The diminution of the activity of the zinc oxide preparation probably resulted from destruction of the more active spots by reduction.

For bulk zinc oxide a very small pressure of water vapor would thermodynamically render reduction impossible at these temperatures. Even at 419° this pressure is only 0.0033 mm.[5] There are two factors which may enter into the observed reduction: (a) thermodynamic considerations applying to bulk material will not apply to surface molecules of different energy characteristics; (b) water vapor is adsorbed so tenaciously as to reduce its vapor pressure below the critical level.

If the surface of the adsorbents be saturated with water vapor after the evacuation but before the start of the determination of the rate of hydrogen adsorption, then the catalyst remains white.

If hydrogen saturated with water at 17° be adsorbed on a freshly evacuated preparation, a fraction of the material at the top of the bulb near the supply tube remains white but that at the bottom turns gray. Thus, during run 51 on preparation 3B at 254°, gas pressure 360 mm., water vapor pressure 7.2 mm., the upper fifth of the zinc oxide remained white, while in run 52 under similar conditions, the upper seventh remained white.

The explanation of this phenomenon is clear. Water vapor is adsorbed so strongly by zinc oxide that the first sections of zinc oxide completely remove the water vapor from the entering gas. Those sections with adsorbed water vapor are protected from attack.

This phenomenon is closely related to one recorded by Russell and Ghering[6] in a study of the effect of oxygen poisoning upon the rate of the hydrogenation of ethylene on copper. There the oxygen was adsorbed tenaciously by the first sections of copper with which it came in contact and portions farther from the inlet tube were supplied only as the nearer portions approached saturation. As a result, progressive additions of oxygen reduced the rate of hydrogenation in a linear manner. As Russell and Ghering emphasize, such a linear relation is not an argument for a uniform surface. From the evidence presented by the present authors, it is clear that similar consideration would prevail in poisoning zinc oxide surfaces with water vapor. In spite of the non-uniformity of zinc oxide surfaces, the reduction of the rate of reaction would bear a linear relation to the quantity of water vapor introduced.

Effect of Water Vapor on the Rate of Activated Adsorption.—Experiments were performed which permit comparison of the rates of activated adsorption of hydrogen and carbon monoxide on zinc oxide surfaces previously saturated with water vapor with those obtained on the ordinarily evacuated catalyst. Adsorption measurements were made at 1 atm. pressure on preparation 3C.

As Taylor and Sickman[3] found, the first portions of water vapor are adsorbed on zinc oxide with great rapidity, the later portions more slowly. Thus, at 218°, preparation 3C, after evacuation for five hours at 410°, adsorbed 7.4 cc. (N. T. P.) of water vapor under 14.5 mm. pressure within two minutes. Another 7.4 cc. was adsorbed in an hour. The final pressure of water vapor was 6 mm.

Table I exhibits the effect of water vapor on the rate of activated adsorption of hydrogen and carbon monoxide on preparation 3C.

TABLE I

EFFECT OF WATER VAPOR ON THE RATE OF ADSORPTION OF HYDROGEN AND CARBON MONOXIDE ON PREPARATION 3C AT 218°

Time, min.	Adsorption in cc. of								
	Hydrogen						Carbon monoxide		
	Run 52	54	55	56	58	59	62	64	65
1	2.35	2.70	2.80		0.40	1.95	0.80	0.90	0.50
2	2.70	3.00	3.10	3.60		2.25	1.10	1.15	.55
4	3.00	3.35	3.30	3.90		2.50	1.65	1.60	.65
8	3.40	3.75	3.60	4.25		2.85	2.30	2.15	.85
12	3.60	4.00	3.85	4.40		3.00	2.80	2.55	1.00
20	3.95	4.30	4.25	4.70	.45	3.30	3.50	3.05	1.15
40	4.35	4.85	4.65	5.05	.50	3.70	4.55	4.10	1.55
60	4.65	5.05	4.90	5.30		3.95	5.20	4.70	1.75
100	4.95	5.45	5.15		.60	4.20	6.00	5.45	2.10

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[5] G. B. Taylor and Starkweather, THIS JOURNAL, **52**, 2323 (1930). This paper deals thoroughly with the problem of reduction of zinc oxide by hydrogen.

[6] Russell and Ghering, *ibid.*, **57**, 2544 (1935).

Adsorption runs 58 and 65 on preparation 3C were performed on zinc oxide surfaces which had been saturated with water vapor in the manner just described. The other runs were made on freshly evacuated surfaces. The gases employed in runs 52, 54, 58, 59, 62, 64 and 65 were free from water vapor. The hydrogen employed in run 55 contained 4.5 mm. of water vapor and that in run 56, 14.5 mm.

It is observed that rates of adsorption of both hydrogen and carbon monoxide are markedly smaller on surfaces saturated with water vapor. On the other hand, partial pressures of water vapor up to 14.5 mm. may be introduced with hydrogen without sensibly affecting the rate of adsorption. At 218° the dead space in the catalyst bulb of preparation 3C amounts to about 20 cc. In run 56, this 20 cc. of gas contains 0.4 cc. (N. T. P.) of water vapor. In the light of earlier considerations this entire quantity would be adsorbed immediately but only by those portions of zinc oxide very near the inlet tube. Since about 7.4 cc. of water vapor can be absorbed with great tenacity, from 5 to 10% of the surface is in the condition of the whole surface in run 58, whereas the remainder of the surface is unaffected. Such variation is within the experimental error set by the reproducibility of the surface.

Similar results were obtained on preparation 3B in regard to the effect of water vapor on the rate of adsorption of hydrogen. At 254° and 0.5 atm. pressure, preliminary saturation of the surface with water vapor reduced the rate of adsorption by 75%.

Because, in the presence of nickel, deuterium exchanges very much more rapidly with benzene than does deuterium oxide, Horiuti and Polanyi[7] consider that the exchange does not proceed by dissociative adsorption succeeded by recombination of the fragments, unless equilibrium conditions on the surface are upset by a change from deuterium to deuterium oxide.

On the basis of common examples of poisoning and on the basis of the researches presented in the paper, the authors consider that water vapor in quantity may reduce reaction rates by reducing the rate of the activated adsorption of the reactants if such adsorption be rate determining, or by making unavailable a certain fraction of the catalytically effective surface if some succeeding step be rate determining. Thus the authors believe that the consideration whereby Horiuti and Polanyi reject the mechanism of exchange via dissociative adsorption is not valid.

Summary

1. Water vapor has been shown to minimize surface reduction of zinc oxide catalysts at lower temperatures.

2. Water vapor has been shown to be strongly adsorbed from gas mixtures containing this vapor by those fractions of zinc oxide surfaces to which the mixture of gases first has access.

3. Saturation of zinc oxide surfaces with water vapor has been shown markedly to inhibit the activated adsorption of hydrogen and carbon monoxide.

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[7] Horiuti and Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

PRINCETON, N. J. RECEIVED JUNE 8, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Behavior of Iodine in Some Sensitized Decompositions of Gaseous Organic Compounds

BY R. FRANCIS FAULL AND G. K. ROLLEFSON

Introduction

It has been shown by Hinshelwood and others[1-3] that the decomposition rates of a number of organic substances are greatly increased by the addition of relatively small amounts of iodine. In discussing their results they have discarded chemical mechanisms for the action of iodine in favor of a hypothesis involving collisions between iodine and the organic molecules. Recently, while preparing to test these reactions for photosensitivity, we have discovered that under the same conditions as prevailed in Hinshelwood's work little or no free iodine can be detected by spectroscopic methods during the course of the reactions. This result leads to the conclusion that these reactions actually proceed by chemical mechan-

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[1] Bairstow and Hinshelwood, *Proc. Roy. Soc.* (London), **A142**, 77 (1933).

[2] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, London, 1933, p. 225.

[3] Bairstow, *Trans. Faraday Soc.*, **29**, 1227 (1933).