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Surface Chemistry of Chromic Oxide

BY SOL W. WELLER AND STERLING E. VOLTZ

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An investigation has been made of the chemical changes that occur on the surface of chromic oxide during oxidation–reduction treatments. A number of adsorption isotherms and isobars of hydrogen and oxygen on differently treated samples of chromia have been determined. The physical adsorption of hydrogen at −78° is greater on reduced than on oxidized chromic oxide, but the difference is much less than the differences in catalytic activities of the two states. Large amounts of hydrogen and oxygen are adsorbed at 500°, only a fraction of which is removable by evacuation at 500°. The hydrogen uptake at 500° is appreciably increased when the concentration of water vapor is reduced to a very low level. The excess oxygen on oxidized chromia can be quantitatively determined by direct iodometric titration. Oxidation–reduction levels for the surface have been established by combination of the excess-oxygen determinations and gas adsorption data. The amount of exchangeable hydrogen, as determined by exchange with gaseous deuterium at high temperature, indicated that some "structural water" was present in the reduced catalyst, in addition to the adsorbed hydrogen. Oxygen exchange studies between chromia and H_2O^{18} at 350° showed exchange occurred to a depth of 2 or 3 atomic layers in a thirty-minute run. A number of cyclic reversible changes that occur during oxidation–reduction treatments also have been investigated. The interrelations between catalytic activity, electrical conductivity, and surface chemistry of chromic oxide are discussed and a schematic representation for the surface is suggested.

Introduction

Previous work[1] has established that the activity of chromic oxide for catalyzing hydrogen–deuterium exchange at low temperatures is greater in the reduced state than in the oxidized state, although the electrical conductivity is greater in the latter. Adsorbed water vapor causes a marked decrease in the catalytic activity, but has practically no effect on the electrical conductivity.[2] These facts indicate that no simple correlation exists between activity and conductivity for chromic oxide. It appeared probable that both the catalytic activity and the electrical conductivity were intimately related to the surface chemistry of chromic oxide, and that the effects of pretreatments on these two properties could only be understood by complete elucidation of the surface chemistry.

The stability of chromic oxide toward reduction[3,4] and oxidation[5–8] at 500° indicates that gross changes in chemical composition or crystal structure should not occur in the bulk material during pretreatment at 500°. There is, however, a variety of evidence in the literature that chemical changes in the surface layer may occur.[9–15]

The adsorption of hydrogen and oxygen on chromia has been investigated by earlier workers.[9–11,13,15] It was considered necessary to repeat and extend these studies, however, partly because of many inconsistencies in the earlier results, and partly to have complete adsorption data on the same batch of chromic oxide which has been used in a number of studies in this Laboratory.

The work of Maslyanskii and Bursian[14] and of Givaudon, Nagelstein and Leygonie[15] on chromia–alumina catalysts implied that chromia contains adsorbed, or excess, oxygen after oxidation and adsorbed hydrogen after reduction. Although only the sum of these quantities can be determined by high temperature gas adsorption, the excess oxygen can be determined separately by an iodometric method, and the adsorbed hydrogen obtained by difference. Both Maslyanskii and Givaudon worked with chromia–alumina catalysts of unknown specific surface of chromia; it was not possible to establish whether the oxidation was limited to the surface. Givaudon and co-workers also studied the water production during an oxidation–reduction cycle, as had been done earlier by Dickinson,[13] as well as the heat effects during cycling. The heat effects were attributed primarily to the formation of water from the adsorbed oxygen or hydrogen, the assumption being made that the heats of adsorption of hydrogen, oxygen and water are relatively small.

In this study, the adsorption of hydrogen and oxygen on chromia has been reinvestigated. Direct measurements of excess oxygen and exchangeable hydrogen have also been made, as well as a study of the reversible changes which occur during successive oxidation–reduction treatments.

Experimental

The purification and drying of the gases and the preparation of the chromia gels employed in this work have been previously described.[1]

Gas adsorption methods were made in two apparatus. One was a static adsorption apparatus (BET),[16] equipped with a cold trap intended to freeze most of the water formed in certain of the experiments, such as hydrogen adsorption on oxidized chromia, and oxygen adsorption on reduced chromia. In the other apparatus, the gas was continuously circulated through a closed system by means of an all glass pump in series with the catalyst sample and a cold trap. In this way, the gas contacting the catalyst was kept dry even during experiments in which water was produced during the adsorption.

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(1) S. E. Voltz and S. W. Weller, THIS JOURNAL, **75**, 5227 (1953).

(2) S. E. Voltz and S. W. Weller, *ibid.*, **75**, 5231 (1953).

(3) F. D. Richardson and J. H. E. Jeffes, *J. Iron and Steel Inst. (London)*, **160**, 261 (1948).

(4) C. G. Meier, *U. S. Bur. Mines Bull.*, No. 436 (1942).

(5) A. Simon and T. Schmidt, *Z. anorg. allgem. Chem.*, **153**, 191 (1926).

(6) I. G. Ryss and A. I. Selyanskaya, *Acta Physicochim.(U.R.S.S.)*, **8**, 623 (1938).

(7) D. S. Datar and S. K. K. Jatkar, *J. Indian Inst. Sci.*, **22A**, 119 (1939).

(8) R. S. Schwartz, I. Fankuchen and R. Ward, THIS JOURNAL, **74**, 1676 (1952).

(9) B. Neumann and E. Goebel, *Z. Elektrochem.*, **40**, 754 (1934).

(10) J. Howard and H. S. Taylor, THIS JOURNAL, **56**, 2259 (1934).

(11) R. L. Burwell and H. S. Taylor, *ibid.*, **58**, 697 (1936).

(12) D. A. Dowden and W. E. Garner, *J. Chem. Soc.*, 893 (1939).

(13) E. J. Dickinson, *Trans. Faraday Soc.*, **40**, 70 (1944).

(14) G. N. Maslyanskii and N. R. Bursian, *J. Gen. Chem. (U.S.S.R.)*, **17**, 208 (1947).

(15) J. Givaudon, E. Nagelstein and R. Leygonie, *J. chim. phys.*, **47**, 304 (1950).

(16) W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Co., Pittsburgh, Pennsylvania, 1949, Chap. XII.

An iodometric method was employed for the determination of the oxidizing material in chromia. A weighed amount (1–2 g.) of the sample was placed in 100 cc. of distilled water, and 20 cc. of concentrated hydrochloric acid was added. Two grams of potassium iodide was then added and the mixture was allowed to stand at least 15 minutes. The brown suspension was then titrated with standard sodium thiosulfate (0.1 *N*); starch solution was added near the end-point.

The water evolved during successive oxidation–reductions at 500° was determined in a flow system. Purified, dried gases were used; the water evolved was absorbed in magnesium perchlorate and weighed.

The relative thermal effects during oxidation and reduction at 500° (0.5 hour on-stream periods in oxygen or hydrogen) were determined by means of a differential chromel-constantan thermocouple connected to a sensitive galvanometer. The thermal effects were taken as proportional to galvanometer deflections.

Weight changes on cycling were determined with a continuous weighing apparatus, adapted from one previously used in this Laboratory for studying quinoline adsorption.[17] Weight changes were corrected for buoyancy effects.

The ethylene hydrogenations were carried out in a static system. In each experiment a fresh charge of catalyst was pretreated in hydrogen or oxygen at 500° and then evacuated for 16 hours, after which it was cooled in vacuum to −78° for testing.

Results

I. Stabilization of Chromia.—Samples of chromia gels, which were prepared from chromic nitrate and ammonium hydroxide and dried at 110°, gave off nitric oxide, nitrogen and carbon dioxide when heated to 750°. It is probable that the nitric oxide and nitrogen result from the decomposition of contaminating nitrate and the carbon dioxide from carbonate formed during the initial precipitation of the chromia gel. These results emphasize the difficulty in obtaining pure chromia from chromia gel and the necessity for caution in attributing results with fresh catalysts to pure chromia. It was for this reason that earlier activity studies[1,2] were carried out with chromia stabilized by cycling in oxygen and hydrogen at 500°. Such cycling gives a product which analyzes 99–100% Cr_2O_3. It has been reported that a sample of chromia heated for two hours at 600° contained 1% water.[18]

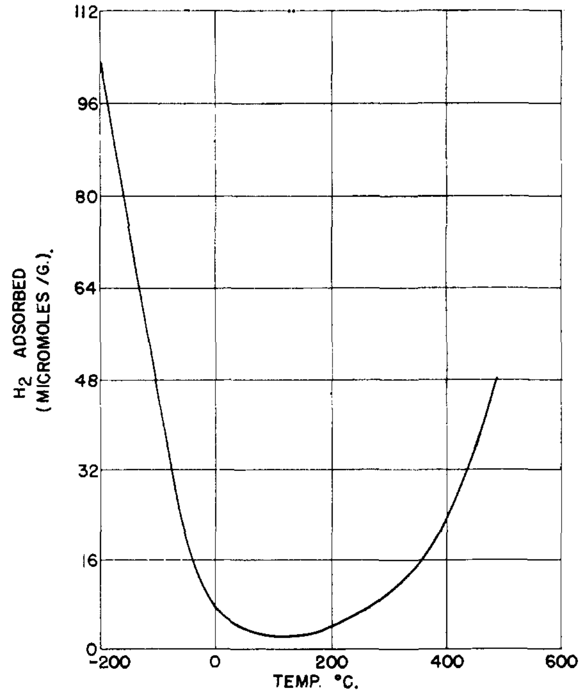

Fig. 1.—Hydrogen adsorption isobar on reduced chromic oxide.

X-Ray diffraction patterns were made of different samples of chromia gel treated with nitrogen, oxygen or hydrogen between 350 and 1000°. In no case were lines observed which could not be attributed to α-chromia. Other oxides, such as γ-Cr_2O_3, Cr_3O_8, Cr_2O_5 or CrO_3,[8,19] were either absent or present as crystallites too small to be detected by X-ray analysis.

Surface area determinations were made on various chromia samples. The chromia gel (dried at 110°) had the high specific surface of 200 m.^{2}/g. This may be compared with the value of 310 m.^{2}/g. reported by Emmett and Cines[20] for a similar chromia gel dried at 150°. Heating the gel in nitrogen at 350° did not affect the area greatly; evacuation at 350° increased the area to 310 m.^{2}/g. Cycling several times in oxygen and hydrogen at 350 or 500° gave a catalyst with an area of 35 m.^{2}/g. Heating to 1000° resulted in a decrease in area to 5 m.^{2}/g.

II. Gas Adsorption.—A number of gas adsorption measurements were made with a chromia gel stabilized by cycling at 500°.

Figure 1 shows the hydrogen adsorption isobar (P_{H_2} = 560 mm.) obtained in the static system after a preliminary reduction and evacuation at 500°. The low temperature branch of the isobar is presumably due to van der Waals forces, although the fact that hydrogen–deuterium exchange activity is observed in this region means that some chemisorption must occur. It is relevant that Beebe and Dowden[21] found the heats of adsorption of hydrogen at −183° to be too high to be accounted for simply on the basis of van der Waals adsorption. A flat minimum in the adsorption occurs in the region 50 to 200°, above which a marked activated adsorption sets in. Howard and Taylor[10] and Burwell and Taylor[11] also found that activated adsorption of hydrogen on chromia gel began in the neighborhood of 50–100°. The quantities of hydrogen they reported chemisorbed at elevated temperatures are larger by a factor of ten than those reported here; however, these investigators employed non-cycled catalyst, which has a much higher surface area than the stabilized oxide. They used the same type of static adsorption apparatus as in the work presented here.

The adsorption isobar shown in Fig. 1 was only studied to 500°; with further temperature increase the amount of chemisorbed hydrogen would presumably increase, reach a maximum, and then decrease as a loss of surface area occurred at high temperatures. It should also be noted that the

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[17] G. A. Mills, E. R. Boedeker and A. G. Oblad, THIS JOURNAL, **72**, 1554 (1950).

[18] M. A. Khachvankyan and B. Ormont, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 575 (1947).

[19] A. W. Laubengayer and H. W. McCune, THIS JOURNAL, **74**, 2362 (1952).

[20] P. H. Emmett and M. Cines, *ibid.*, **68**, 2535 (1946).

[21] R. A. Beebe and D. A. Dowden, *ibid.*, **60**, 2912 (1938).

amounts of hydrogen indicated as adsorbed in Fig. 1 do not include any hydrogen present on the catalyst after the preliminary reduction and evacuation at 500°.

Similar results are shown in Fig. 2 for the oxygen adsorption isobar (P_{O_2} = 490 mm.) on stabilized chromia after preliminary oxidation and evacuation at 500°. Again a minimum is observed around 100°, with a high temperature branch which indicates activated chemisorption. As in the previous case, the amount of adsorbed oxygen shown does not include oxygen which was adsorbed during oxidation and not removed by pumping at 500°.

The adsorption isobars shown in Figs. 1 and 2 were determined in several steps from low to high temperatures. In most instances the adsorption or desorption was fairly rapid and equilibrium (no change for an additional period of one hour) was generally reached within the first hour. This was especially true at lower temperatures; longer periods of time were occasionally required at the higher temperatures. Several individual points were checked after equilibrium was attained for additional periods of 16 hours, and no further adsorption or desorption was observed.

A number of individual adsorption isotherms were determined at 500° for both oxygen and hydrogen on oxidized and reduced chromia. These isotherms are essentially Type I[22]; "saturation" adsorption values are summarized in Table I. In each experiment the chromia was evacuated for 16 hours at 500° between the pretreatment and the adsorption determination. The amounts of hydrogen adsorbed by reduced chromia (evacuated) and of oxygen by oxidized chromia (also evacuated) represent that portion of the total hydrogen or oxygen adsorption which is reversible at 500°. The reversible oxygen chemisorption is the same in the static system and the circulating system. However, all the other adsorptions listed in Table I are dependent on the type of apparatus employed. In the circulating system the gas being adsorbed is continually dried as it is forced through the cold trap; in the static system the drying is less efficient, depending on the diffusion of the water vapor to the cold trap. The magnitudes of the gas consumptions are considerably greater when the water vapor pressure in the gas is maintained at a very low level. This is associated with an increased hydrogen adsorption in dry gas, since the oxygen adsorption is independent of the presence of residual water vapor. The increased hydrogen adsorption in the absence of water vapor may be alternatively expressed as an incipient reduction of chromic oxide to chromous oxide; this will be considered in detail later. Either interpretation is consistent with the observation of Dickinson,[13] confirmed by us, that the addition of water to the reduced catalyst results in the evolution of hydrogen. Dickinson also found that the total hydrogen consumed by his catalyst after oxidation and evacuation was about 1200 micromoles per gram, and that the total oxygen consumed after reduction and evacuation was about 600 micromoles per gram. These figures are about double those obtained in this study, but since the surface area of Dickinson's catalyst is not known, it is not clear whether this discrepancy is real.

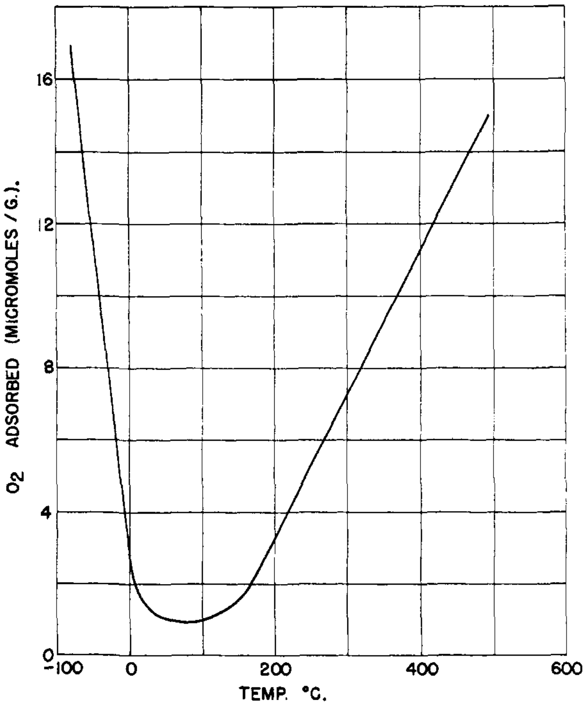

Fig. 2.—Oxygen adsorption isobar on oxidized chromic oxide.

TABLE I

HYDROGEN AND OXYGEN ADSORPTION ON CHROMIA AT 500°

	Static system, μmoles/g.	Circulating system, μmoles/g.
O_2 ads. by oxidized chromic oxide	15	15
H_2 ads. by reduced chromic oxide	55	175
O_2 ads. by reduced chromic oxide	255	300
H_2 ads. by oxidized chromic oxide	555	700

The fact that chemisorption of oxygen and hydrogen occurs at temperatures as high as 500° means that the heats of adsorption must be very high. Howard and Taylor[10] found that the heat of adsorption of the hydrogen *reversibly* adsorbed around 350° was 27 kcal. per mole. Presumably, comparable values obtain for the oxygen which is reversibly adsorbed. Still higher values of the adsorption energies must characterize that gas which is so strongly adsorbed that it is not removed by pumping at 500°.

The adsorption of hydrogen at low temperatures was studied in order to determine whether the influence of pretreatment on catalytic activity for hydrogen–deuterium exchange[1] was directly related to the amount of hydrogen adsorbed at low temperatures. A number of individual isotherms were determined in the static system, and the results are summarized in Fig. 3. The hydrogen adsorption at low temperatures is greater after reduction and evacuation at 500° than after oxidation and evacuation at 500°. The twofold difference in adsorption between oxidized and reduced chromia is not sufficient to account for the difference in catalytic activity for hydrogen–deuterium ex-

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[22] S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, THIS JOURNAL, 62, 1723 (1940).

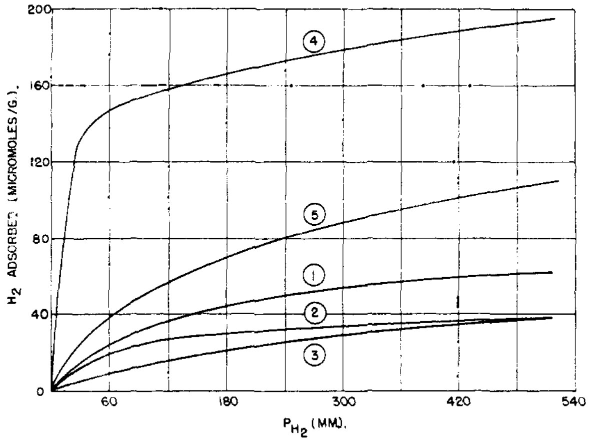

Fig. 3.—Low-temperature hydrogen adsorption isotherms: 1 and 4, H_2 and evac. at 500°; 2 and 5, O_2 and evac. at 500°; 3, H_2 at 500 and evac. at −78°. Adsorption temperatures: 1, 2 and 3 at −78°; 4 and 5 at −195°.

change. The adsorption at −78° is also greater after reduction and evacuation at 500° than after reduction at 500° and evacuation at −78°, which is in agreement with the finding of Howard[23] that hydrogen adsorbed on chromia at elevated temperatures decreases the adsorption of hydrogen at −78°. Howard's result was not confirmed by Emmett and Cines,[20] but these workers dried their gel only at 150°, while Howard used a temperature of 400°. The effect found by Howard and in this work is a reasonable one. The adsorption at −78° is on the tail end of the van der Waals section of the isobar (Fig. 1), where the surface coverage is low and may be expected to be sensitive to variations in the heat of adsorption. The heat of adsorption is determined not only by the nature of the physically adsorbed gas, but also by the effective polarizability and the "characteristic energy" of the adsorbent,[24] both of which should be influenced by gas previously chemisorbed on the solid. It is of interest in this connection that Stone and Tiley[25] have found the krypton adsorption on copper oxide at −183° to be affected by the prior chemisorption of carbon monoxide at room temperature.

III. Chemical Studies of Catalyst Oxygen and Hydrogen.—It was found that the excess oxygen on oxidized chromia could be determined by an iodometric method directly on the solid, without employing the preliminary Soxhlet extraction used by Givaudon and co-workers.[15] This eliminated the potential error that a non-extractable, higher-valent chromium oxide might be present on the surface and not determined. The results obtained on chromia by this method are given in Table II.

TABLE II

EXCESS OXYGEN ON CHROMIA

Treatment	Excess oxygen, μmoles/g.
Chromia gel dried at 110° only	3
Cycled gel[a] after O_2 at 500°	141
Cycled gel after O_2 and evac. at 500°	110
Cycled gel after H_2 at 500°	6
Cycled gel after H_2 at 500°, evac. at 500°, O_2 at 350°	104

[a] Stabilized by cycling several times in hydrogen and oxygen at 500°.

Chromia, prepared from chromic nitrate and ammonium hydroxide and dried only at 110°, does not contain appreciable amounts of excess oxygen. This is contrary to the belief, occasionally stated in the literature, that the black color of such gels is caused by the presence of large amounts of higher-valent chromium oxides. Oxidation at 500° of stabilized chromia introduces about 140 micromoles excess oxygen per gram chromia. If a cross-sectional area of 6.8 Å.[2] (the value for close-packed oxide ions) is assumed for each adsorbed atom, this corresponds to a surface coverage of 11 m.^{2}/g., or about one-third of the total surface (35 m.^{2}/g.). After evacuation at 500°, 110 micromoles oxygen per gram remained on the chromia, which implies that about 30 micromoles per gram of the oxygen adsorbed at 500° is removed by evacuation. This is reasonably consistent with the value of 15 micromoles per gram obtained from gas adsorption measurements. Within the experimental error of the method, reduced chromia does not contain excess oxygen. Oxidation at 350° of stabilized and reduced chromia does not introduce as much oxygen as oxidation at 500°.

As a result of this work, it was hoped that it might be possible to establish a quantitative relationship between the excess oxygen introduced at 500° and the specific surface area of chromia in a chromia-containing catalyst. Such a relationship would be of great utility in determining the fraction of the total surface area of supported chromia catalysts which could be attributed to the chromia alone; this quantity has heretofore been calculable only very indirectly from measurements of magnetic susceptibility.[26] To investigate this point, separate samples of stabilized chromia were heated in air for eight hours at temperatures between 500 and 1000° in order to effect changes in area. The surface area and excess oxygen content of each sample were determined; retreatment with oxygen at 500° did not further increase the excess oxygen content. The ratio of surface area to excess oxygen for six samples, which had a range of surface areas of 5–35 m.^{2}/g., was 0.163 m.^{2}/μmoles with a standard deviation of 0.051 m.^{2}/μmoles. From these data, it appears that this method will give only an approximate measure of the specific chromia area in supported catalysts.

A number of attempts were made to determine adsorbed hydrogen on reduced chromia by aqueous titration with potassium permanganate, potassium dichromate and bromine water. In no case was the presence of oxidizable hydrogen detected by such procedures.

The total amounts of exchangeable hydrogen present on various chromia samples were determined by equilibrating the samples with pure deuterium in a static system. Chromia which had been reduced and evacuated at 500° contained 382 ± 2 μ moles exchangeable hydrogen per gram. No ex-

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[23] J. Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

[24] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., Chap. VII, 1943.

[25] F. S. Stone and P. F. Tiley, *Nature*, **167**, 654 (1951).

[26] R. P. Eischens and P. W. Selwood, THIS JOURNAL, **69**, 1590, 2698 (1947); **70**, 2271 (1948).

change occurred between this chromia sample and gaseous deuterium at −78°. Reduced chromia cooled in hydrogen and evacuated only at −78° also did not exchange with deuterium at −78°. In the last two cases, the catalyst is known to contain chemisorbed hydrogen, which thus does not exchange with gaseous deuterium under conditions where hydrogen–deuterium exchange is very well catalyzed. This behavior is exactly analogous to that reported by Kummer and Emmett[27] for singly promoted iron catalysts.

Attempts were made to determine "active" hydrogen by reaction of both oxidized and reduced chromia, evacuated at 500°, with Zerewitinoff reagent, methylmagnesium iodide, at 25 and 100°. Reduced, evacuated (500°) chromia reacted to the extent of 76 μmoles "active" hydrogen per gram at 25° and 153 at 100°; oxidized, evacuated chromia gave a test for 173 μmoles "active" hydrogen per gram at 100°. Since the apparent "active" hydrogen increases as the temperature of the reaction with methylmagnesium iodide is increased, these values can only be considered to be minimum figures. Karl Fischer analyses for "free" water on similar samples gave zero values, within experimental error.

Duplicate determinations of ignition loss on chromia reduced and evacuated in a static system gave an average value of 0.75% weight loss on ignition. If only water is evolved on ignition, this is equivalent to 416 μmoles hydrogen per gram chromia.

Samples of chromia, cycled at 350°, were tested for oxygen exchange with H_2O^{18} containing 1.6 atom per cent O^{18}.[28] A weight of 0.3 to 0.4 g. of H_2O^{18} in a nitrogen carrier stream was passed over 2 g. of catalyst at 350° during a 30-minute run. Mass-spectrometric analysis of the product water showed that about 10% of the total catalyst oxygen exchanged, both for preoxidized or prereduced chromia. This corresponds to a penetration of 2–3 atomic layers.

Studies of Reversible Changes on Cycling.—The weight changes suffered by stabilized chromia on cycling in oxygen and hydrogen were determined at 500 and 350°. At 500°, the sample gained 0.25% in weight (in the steady state) on changing from a flowing hydrogen to a flowing oxygen atmosphere, and it lost a like amount on changing from oxygen to hydrogen. At 350°, the weight changes were smaller and in the *reverse* direction; a weight *loss* of 0.07% occurred on oxidation, and a corresponding *gain* on reduction. This is almost certainly due to differences, as a function of temperature, between the retention of water by the reduced and oxidized forms at the chromia. These results emphasize the complexity of a quantity such as weight change, which is the resultant of a number of factors simultaneously operative.

The average amount of water evolved by stabilized chromia during cycling at 500° in a flow system was about 350 μmoles water per gram chromia during hydrogen treatment and 330 in oxygen, the total for a complete cycle being 680 μmoles per gram. In both atmospheres, all the water was evolved within one hour, and no appreciable water was evolved during the intermediate nitrogen flush.

The thermal effect observed on changing from flowing oxygen to flowing hydrogen at 500° was about four times greater than that observed on changing from hydrogen to oxygen. Givaudon and co-workers reported similar results for a chromia–alumina catalyst.[15]

Discussion

The fact that low temperature hydrogen–deuterium exchange occurs[1] implies that some hydrogen is reversibly chemisorbed at low temperature (−78°). This hydrogen, however, is not equivalent to the hydrogen chemisorbed at high temperature (500°), as evidenced by the failure of the hydrogen adsorbed at 500° to participate in the exchange reaction at −78°. With chromia, therefore, just as with iron catalysts,[27] at least two types of chemisorption of hydrogen occur.

From a consideration of the adsorption data and the excess oxygen values determined by direct iodometry, the oxidation–reduction levels of the chromia surface can be deduced. The oxidized chromia contained 140 μmoles excess oxygen per gram, as determined by iodometric titration. Since evacuation at 500° removed about 15 μmoles oxygen per gram, the oxidized and evacuated sample contained 140 − 15 = 125 μmoles excess oxygen per gram. The material in this condition reacted with 700 μmoles hydrogen per gram in a very dry system (555 μmoles in a static system). Therefore, the reduction level for reduced chromia in very dry hydrogen is 700 − 2 (125) = 450 μmoles hydrogen per gram (305 μmoles in a static system). The reduction level for reduced chromia after evacuation at 500° is less than this value by the amount of reversibly adsorbed hydrogen; for the catalyst reduced in very dry hydrogen, the reduction level after evacuation is, then, 450 − 175 = 275 μmoles hydrogen per gram, and in the static, 305 − 55 = 250 μmoles per gram.

These oxidation–reduction levels are schematically presented in Fig. 4. Part A represents the situation when the circulating system (very dry hydrogen) was used; part B, when the static system was used. The significance of the values shown can be better appreciated by comparison with the total surface of the sample. Like many oxides, chromia has essen-

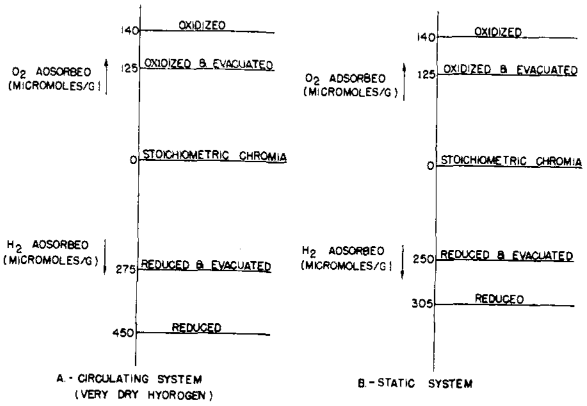

Fig. 4.—Schematic representation of the oxidation–reduction levels of chromic oxide.

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[27] J. T. Kummer and P. H. Emmett, *J. Phys. Chem.*, **56**, 258 (1952).

[28] The authors are very grateful to Dr. S. G. Hindin for carrying out the experiments on oxygen exchange.

tially a close-packed structure of oxide ions, with an oxide ion cross-section of about 6.8 Å.[2] On this basis, the chromia used in this work, which has a surface area of 35 m.^{2}/g., would have in its surface 855 μgram atoms, or 428 μmoles of oxygen per gram. The amount of hydrogen sorbed by reduced chromia under very dry conditions corresponds to a ratio of 900:855, or approximately 1:1, of hydrogen atoms to surface oxide ions. In a static system this ratio is smaller.

In a similar way, the amount of excess oxygen on oxidized chromia is sufficient to cover about one-third of the surface with a close-packed layer of oxide ions. In reality, there is probably a rearrangement of the lattice structure in the surface layers to something resembling chromium trioxide or some other higher valent oxide, as some of the trivalent chromium ions become converted to higher valent ions.

Several cross-relations exist which can be used to test the consistency of the oxidation–reduction levels shown in Fig. 4. In the first place, the total oxygen required to oxidize reduced and evacuated chromia should equal half of the hydrogen adsorbed in the reduced state plus the oxygen adsorbed in the oxidized state. In very dry hydrogen this should be $275/2 + 140 \fallingdotseq 278$ μmoles oxygen per gram and in a static system $250/2 + 140 = 265$. The observed oxygen adsorptions were 300 and 255 μmoles oxygen per gram, respectively. Secondly, the total amount of water produced in a hydrogen–oxygen cycle (dried gases) should equal $450 + 2\ (140) = 730$ μmoles water per gram; the amount obtained by direct determination was 680 μmoles per gram. In view of the experimental inaccuracies, the internal consistency of the data is reasonable.

More water was evolved during the hydrogen treatment of the oxidized catalyst (350 μmoles water per gram) than can be accounted for if only the excess oxygen were removed (2 × 140 μmoles water per gram). This means that either some "combined water" which is present in the oxidized state is evolved on hydrogen adsorption, or some of the hydrogen adsorbed on stoichiometric chromic oxide comes off with oxygen from the catalyst to give water and the equivalent of chromous oxide.

The exchangeable hydrogen, as measured with deuterium at high temperature, is probably the best measure of the total hydrogen in the chromia; it should include both adsorbed hydrogen and that present as "structural water." The value of 382 μmoles of exchangeable hydrogen per gram obtained for chromia reduced in a static system and evacuated is greater than the 250 μmoles of adsorbed hydrogen per gram believed to be present. The excess, about 130 μmoles per gram, is presumably to be attributed to "structural water." It had been hoped that the Zerewitinoff method for active hydrogen would furnish additional information on this point, but this method gave inconclusive results. The Karl Fischer analysis indicated that "free water" was absent, but the applicability of this method to high area, insoluble solids such as chromia is questionable.

The interpretation given by Givaudon and coworkers to the thermal effects observed on cycling chromia catalysts appears to be oversimplified. If the galvanometer deflections are proportional to the heat liberated in each step, the ratio of heat evolved on reduction to that evolved on oxidation is about 4:1. However, as inspection of Fig. 4 shows, if the heat evolution were due exclusively to the production of water from adsorbed oxygen or hydrogen, this ratio would be expected to be 2(140):450, or 1:1.6. This discrepancy seems to require one or both of the following explanations: (1) if all the water formed in each treatment comes off the catalyst, the heats of adsorption of hydrogen and oxygen must be relatively high and must differ appreciably; and (2) a different fraction of the water formed remains on the reduced than on the oxidized catalyst, and the heat of adsorption of water is high. In view of the earlier discussion, it seems certain that the heats of adsorption of hydrogen, oxygen, and water are indeed high, and both (1) and (2) may play important roles.

It is of interest to consider the average particle diameter in the stabilized catalyst studied. For uniform spherical particles

$$d(\text{Å.}) = \frac{6 \times 10^4}{\rho(\text{g./cc.}) \times S(\text{m.}^2/\text{g.})}$$

where d is the particle diameter, ρ is the density and S is the specific surface area. The density of the chromia, determined by water immersion, was 5.1 g./cc. Since the surface area of the catalyst was 35 m.^{2}/g., the (equivalent) average particle diameter was 335 Å.

It is clear that marked chemical changes can take place in the surface layers of chromia during various pretreatments. In the presence of oxygen at elevated temperatures, significant quantities of oxygen are strongly bound to the surface, creating, in effect, a partial surface layer of a higher valent oxide such as chromium trioxide. In the presence of hydrogen at high temperatures, correspondingly large quantities of hydrogen are bound. It appears that the amount of hydrogen taken up by the chromia is a function of the partial pressure of the water vapor in the hydrogen, and it is reasonable that this should be so. Insofar as the stoichiometry is concerned, the adsorption of hydrogen on chromia is equivalent to the partial reduction of the chromia surface to chromous oxide; as the following equation indicates, the only difference lies in whether water is removed from the chromia

$$Cr_2O_3 + H_2 \longrightarrow Cr_2O_3{\cdot}H_2 = 2CrO{\cdot}H_2O \longrightarrow 2CrO + H_2O$$

Thermodynamic data for *bulk* chromous oxide[4] show that *bulk* chromia may be reduced to chromous oxide at 500° by hydrogen at atmospheric pressure if the water partial pressure is kept below about 0.017 mm. Although the thermodynamics are presumably different for chromia in a surface or in very small crystallites than for bulk chromia, the extent of surface reduction, *i.e.*, of hydrogen adsorption, in laboratory experiments may reasonably depend on the dryness of the hydrogen in a range likely to be encountered.

Reduced chromia was found to be more active for hydrogen–deuterium exchange and to have lower electrical conductivity than oxidized chromia.[1] Similar catalytic behavior has since been observed for ethylene hydrogenation. Chromia reduced and evacuated at 500° is quite active for ethylene hydrogenation at −78°, while the oxidized and evacuated catalyst is inactive. Presumably in this case also, as in the case of hydrogen–deuterium exchange, the preconditioned state of catalyst is not altered during the low temperature hydrogenation reaction.

It is not surprising that no simple correlation exists between catalytic activity and electrical conductivity. The conductivity is, in a sense, a measure of lattice defects. In the case of chromia, however, the defects which increase the conductivity are the excess oxygen atoms on the surface. These atoms occupy catalytically active surface sites and thereby effectively poison the catalyst for the activation of hydrogen. It is significant that to obtain even a very low exchange activity at −78° with oxidized chromia, it was necessary to remove part of the adsorbed oxygen by evacuation at 500°; otherwise, oxidized chromia was completely inactive.[1] The effect of water as a poison[2] may be interpreted in a similar manner: crudely speaking, the same active sites which are able to bind excess oxygen are also able to adsorb water strongly, and thus lose their activity. Since more active sites are present in the reduced chromia than in the oxidized material after evacuation, higher concentrations of water are necessary to poison the reduced than oxidized chromia.[2]

The nature of the active sites remains a matter of speculation at the present time. It is probable that the surface of oxides like chromia is largely made up of hydroxyl groups when exposed to water. Evacuation at high temperatures removes water, presumably from surface hydroxyl groups, and may leave the surface in a "strained," and therefore reactive, condition.[29]

Figure 5A is a very schematic representation of the surface of reduced, evacuated chromia in the neighborhood of an active site (depicted in (A) as the boxed chromic ion). Chemisorbed excess oxygen is assumed to occupy these sites, as indicated in Fig. 5B. The adsorbed oxygen atoms become oxide ions by the extraction of electrons from a stoichiometrically equivalent number of chromia ions, which become higher valent ions (schematically represented in Fig. 5 as hexavalent ions). It is the simultaneous presence of trivalent and higher valent chromium ions which is responsible for the high conductivity in this condition, since the electronic shifts indicated in (B) $\rightleftarrows$ (C) occur readily. Adsorbed water is assumed to occupy the same positions as adsorbed excess oxygen; this is shown schematically in Fig. 5D. In this case, however, although the catalyst is deactivated, no increase in conductivity occurs since no higher valent chromium ions are formed.

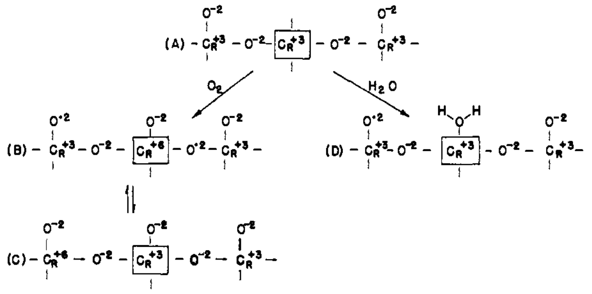

Fig. 5.—Chromic oxide surface (schematic representation).

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MARCUS HOOK, PA.

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Surface Chemistry of Chromia–Alumina

BY STERLING E. VOLTZ AND SOL W. WELLER

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The changes in surface composition of a chromia–alumina catalyst (20% Cr_2O_3) which occur on oxidation and reduction have been studied by gas adsorption and aqueous titrations; in this way quantitative values have been established for the oxidation–reduction levels of the surface. The amount of excess oxygen adsorbed on oxygen treatment at 500° is comparable, on a catalyst weight basis, with that adsorbed by an unsupported chromia catalyst. To the extent that the excess oxygen is a measure of the *chromia* area, the chromia is about three times more efficiently distributed in the supported than in the unsupported catalyst. Very little hydrogen is chemisorbed by the supported catalyst at 500°, and the physical adsorption of hydrogen at −78° is less than the experimental error. Measurements have also been made of the weight changes, water evolution, and thermal effects accompanying oxidation–reduction cycles at high temperature. Interpretation of the weight changes and thermal effects is complex, since these quantities are resultants of several simultaneous processes.

Introduction

The catalytic behavior of chromia–alumina for hydrogen–deuterium exchange is analogous to that of unsupported chromia; the reduced state is more active than the oxidized state.[1] In the case of chromia, the variance in activities exhibited in these two states appears to be closely associated with the gross chemical changes that take place in the surface during oxidation and reduction at high temperature.[2] Detailed studies of the surface chemistry of chromia have resulted in the establishment of quantitative oxidation–reduction levels for the surface.[2] This type of investigation has been extended to a commercial chromia–alumina catalyst

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(2) S. W. Weller and S. E. Voltz, *ibid.*, **76**, 4695 (1954).