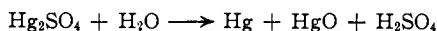
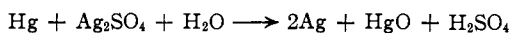


0.0008 M H_2SO_4 is sufficient to prevent formation of the basic salt at room temperature. Hence a mercurous sulfate electrode in 0.05 M H_2SO_4 should attain the theoretical potential against a silver sulfate electrode. This was observed in the present work. To check on the behavior of mercurous sulfate solutions at higher temperatures an aliquot of saturated mercurous sulfate solution in 0.05 M H_2SO_4 was sealed in a small Pyrex tube and heated to 250°. Small yellow crystals of what appeared to be HgO formed on the side of the tube. They were probably formed by the reaction



In the case of Ag_2SO_4 no basic hydrolytic product has been reported. To check on this, a quantity of Ag_2SO_4 and water was sealed in a silica tube and heated to 250°. Visual observation revealed no change in the appearance of the Ag_2SO_4 crystals up to 250°, and the crystals contained the 2:1 ratio between Ag^+ and SO_4^{2-} after cooling. Hence, it does not hydrolyze appreciably under the conditions of the experiment.

If the mercurous sulfate disproportionates and hydrolyzes at higher temperatures the cell reaction becomes, in the limit



ΔF for this reaction is about +12,560 cal., which gives a value for E of -272 mv. ΔS for the reaction is -41.0 e.u., hence $dE/dT = -0.89$ mv./degree. Examination of the equation indicates that higher sulfuric acid concentrations will tend to repress this reaction and hence favor the simple reaction $2Hg + Hg_2SO_4 \rightarrow 2Ag + Hg_2SO_4$. This is what was observed experimentally. In 0.5 M H_2SO_4 the experimental plot coincided with the calculated plot over the temperature range studied, while in the lower acid concentrations the potential of the Ag_2SO_4 electrode was more negative than predicted.

It was not possible to extend the runs in 0.5 and

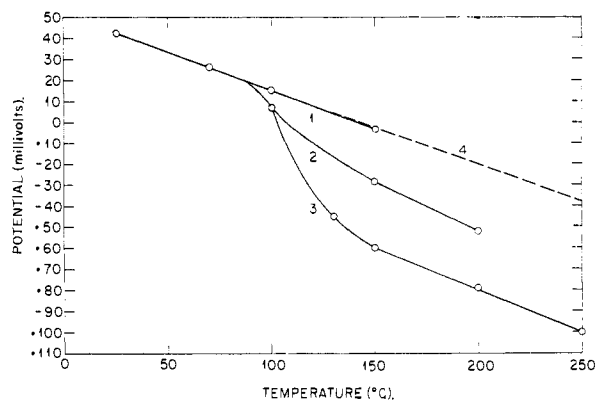
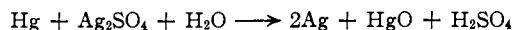


Fig. 1.—The potentials obtained with the silver-silver sulfate and the mercury-mercurous sulfate electrodes as a function of temperature: 1, electrodes in 0.5 M H_2SO_4 ; 2, electrodes in 0.2 M H_2SO_4 ; 3, electrodes in 0.05 M H_2SO_4 ; 4, theoretical plot for the electrodes with no hydrolysis.

0.2 M H_2SO_4 to higher temperatures because the H_2SO_4 attacked the silver above 150 and 200°, respectively, and destroyed the electrodes. The run in 0.05 M H_2SO_4 was not extended above 250° because the Teflon used as a plug and as an insulating coating on the wires is known to soften just above 250°.

It is proposed that at 25 and up to about 100° the potential of the electrode pair corresponds to the reaction $2Hg + Ag_2SO_4 \rightarrow 2Ag + Hg_2SO_4$. Above 100° this is also the cell reaction in sufficiently high H_2SO_4 concentrations. In lower acid concentrations it is proposed that the potential corresponds to a combination of this reaction and the reaction



It is probable that as the temperature is raised this reaction is approached as a limit after perhaps several stages of basic salt formation.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Catalytic Activity and Electrical Conductivity of Chromic Oxide Catalysts

BY STERLING E. VOLTZ AND SOL WELLER

RECEIVED APRIL 27, 1953

A study has been made of the electrical conductivity and catalytic activity of chromia and chromia-alumina catalysts. The catalysts were pretreated with hydrogen or oxygen at high temperature and evacuated at various temperatures before measurement. In agreement with literature reports, the conductivity was found to be much higher in the oxidized than in the reduced state. The activation energy for conduction was about 10 kcal./mole in the oxidized state and 40 kcal./mole in the reduced state. Hydrogen-deuterium exchange at low temperatures (-78 or -195°) was used as a measure of catalytic activity; the oxidation-reduction state of the catalyst was not changed by the reaction. Contrary to what might be expected, the catalytic activity was greater in the reduced than in the oxidized state, although the concentration of "defects" leading to conductivity is greater in the latter condition.

Introduction

This report is the first of several to appear on work being done in these laboratories on the electrical, chemical and catalytic properties of certain transition metal oxides. One of the objectives has been to extend the range of experimental knowledge of semi-conducting oxides in order that current theories relating catalysis and electronic structure may be

adequately tested.¹⁻³ This paper is concerned primarily with the electrical and catalytic properties of chromia and chromia-alumina catalysts; a study of

- (1) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).
- (2) C. Wagner, *J. Chem. Phys.*, **18**, 69 (1950).
- (3) W. E. Garner, T. J. Gray and F. S. Stone, *Proc. Roy. Soc. (London)*, **A197**, 294 (1949); **A211**, 472 (1952); *Discussions Faraday Soc.*, **8**, 246 (1950).

the surface chemistry of chromia will be presented subsequently.

Two alternatives are open to the investigator desiring to study the relation between the electrical and the catalytic properties of the transition metal oxides. Either he may prepare separate samples of different chemical composition, varying in conductivity because of incorporation of small amounts of oxides of metals of different valencies^{4,5}; or he may study a single sample, pretreated in different ways to vary its state of conduction.⁶ The first course of action is subject to several difficulties: it is frequently difficult to reproduce catalytic activity with separate samples; values of electrical resistance, which depend on compactness of interparticle packing, may also be difficultly reproducible with separate samples; and the use of high temperatures to achieve chemical homogeneity of mixed oxides may result in materials of such low surface area that their catalytic activity is difficult to measure. For these reasons the second alternative, involving varying pretreatment of a single sample, was chosen for the work reported here.

Experimental

Materials.—Chromic oxide was prepared by the slow addition of dilute ammonium hydroxide to chromic nitrate solution with vigorous stirring.⁷ The solution was allowed to stand for several days, filtered, washed with warm water until negative nitrate and carbonate tests were obtained on the washings, and then air dried at 110° for eight hours. Chemical analysis showed this material to be 67.8% chromic oxide; X-ray diffraction studies indicated that it was completely amorphous, and its surface area was 124 m.²/g. (BET method).

The chromia-alumina catalyst studied contains 20% chromia supported on γ -alumina; its surface area is 50 m.²/g. This is standard Houdry Type R catalyst, used commercially for butadiene production.

Dried tank hydrogen was purified by passage over palladium on alumina at 250 to 300° followed by a silica gel trap at -195°. Oxygen was dried by passage through calcium sulfate.

Two tanks of deuterium from the Stuart Oxygen Company were used; the analyses by mass spectrograph were 99.5% deuterium, 0.5% hydrogen deuteride and 98.2% deuterium, and 1.8% hydrogen deuteride.

Helium, which was employed for calibration of catalyst volumes and cooling of catalysts, was purified by passage through a charcoal trap at -195°.

Apparatus and Procedure.—Electrical conductivity was measured by placing the powdered catalyst between two electrodes and applying a direct current potential not exceeding 3 volts. Measurements were made with a Wheatstone bridge or Hickok vacuum-tube voltmeter. Voltage was applied to the sample only during the measurement of conductivity in order to minimize polarization effects.

Preliminary measurements of the dependence of conductivity on temperature and gas composition were made in a flowing system at atmospheric pressure. In these experiments the catalyst was placed between perforated platinum electrodes; the upper one was weighted with a perforated stainless steel cylinder. Catalytic activities and conductivities were also determined simultaneously with the use of a high vacuum system; in this case the catalyst was placed between two concentric gold-plated brass cylinders. An all-glass, electromagnetic circulating pump was employed to cycle gas through the powdered catalyst. Provision was also made for taking small samples of the circulating gas during the course of an experiment for analysis by mass spectrometer.

In a typical experiment 7 g. of catalyst was heated to the temperature of pretreatment (350 or 500°) under vacuum. Oxygen (or hydrogen) was admitted and circulated over the catalyst for three hours; the catalyst was then evacuated for one hour and retreated with oxygen (or hydrogen) for three hours. The catalyst was finally pumped, at pretreatment temperature, for 16 hours and cooled under helium to -78 or -195°, at which temperature the hydrogen-deuterium exchange was studied at 400 mm., after removal of the helium. The reactor section had a calibrated volume of approximately 200 cc. (STP) with the catalyst at -78°. The first gas sample was taken for analysis after ten minutes reaction time. At the conclusion of the exchange experiment the catalyst was evacuated at low temperature and was heated to pretreatment temperature under vacuum. The exchange studies were carried out with a 1:1 hydrogen-deuterium mixture.

Results

Dependence of Conductivity on Temperature and Gaseous Atmosphere.—The electrical resistance of chromic oxide was measured as a function of gas atmosphere and of temperature. For each atmosphere, excellent straight line plots were obtained for $\log R$ versus $1/T$. The calculated activation energies for conduction are shown in Table I.

TABLE I
ACTIVATION ENERGIES FOR CONDUCTION

Gas	O ₂	Air	N ₂	H ₂
<i>E</i> , kcal./mole	9.8	9.8	10.8	39.9

The results confirm those of Bevan, Shelton and Anderson⁶ for a sintered chromia sample, the resistances increasing in the order: oxygen \approx air < nitrogen << hydrogen. Water caused only a slight increase in resistance in oxygen, air, or nitrogen, and it exerted no measurable effect in a hydrogen atmosphere. Exposure to ultraviolet radiation or X-rays had no effect on the conductivity of chromic oxide. No fluorescence was noted in either case.

Catalytic Activity as a Function of Pretreatment.

—It was originally intended to employ a hydrocarbon reaction such as cyclohexane dehydrogenation to study the activity-conductivity relationship. Unfortunately, it became clear that at the temperatures necessary for appreciable reaction (450 to 500°), the reacting gases rapidly exerted a "leveling effect" on the catalyst; as soon as the reaction started, the catalyst was brought to the same state of reduction and conductivity regardless of its pretreatment. It became necessary, therefore, to find some reaction, catalyzed by chromia, which proceeded at temperatures so low that the state achieved by pretreatment would not be changed by the reaction. The hydrogen-deuterium exchange, H₂ + D₂ = 2HD, was found to be such a reaction, and it was used in all further work. The exchange reaction has the additional virtues of being relatively simple and of providing information on the mechanism whereby molecular hydrogen is activated.

Attempts to carry out pretreatment at 350° followed by hydrogen-deuterium exchange at -78° resulted in reproducible conductivity values, but poorly reproducible catalytic activities. It was assumed that this behavior resulted from difficulty in removing adsorbed water by evacuation at 350°.

As a result of the poor reproducibility obtained with catalysts pretreated at 350° activity was investigated as a function of pretreatment at 500°. Prior

(4) E. J. W. Verwey, P. W. Haayman, F. C. Romeyn and G. W. Van Gosterhout, *Phillips Research Reports*, **5**, 173 (1950).

(5) W. A. Weyl and T. Förland, *Ind. Eng. Chem.*, **42**, 257 (1950).

(6) D. J. M. Bevan, J. P. Shelton and J. S. Anderson, *J. Chem. Soc.*, 1729 (1948).

(7) W. A. Lazier and J. V. Vaughen, *THIS JOURNAL*, **54**, 3080 (1932).

to these experiments, the chromic oxide catalyst was subjected to several cycles of oxygen and hydrogen treatment at 500° in order to put it in a "steady state" condition with respect to composition and surface area. Salley, Fehrer and Taylor had indicated that chromic oxide gels could, by careful treatment, remain stable and active up to 600°. A similar result was obtained in these experiments; the chromic oxide catalyst cycled at 500° was still active, and different preparations had surface areas of 15 to 35 m.²/g. after cycling. The color of the catalyst was dark green-black in the oxidized condition and bright green in the reduced condition, the color changes being reversible at 500°; as pointed out by Salley, Fehrer and Taylor, the green color is not a definitive indication of the occurrence of an irreversible "glow phenomenon." X-Ray diffraction patterns of the cycled catalyst showed the presence of very small crystallites of α -chromia.

Table II contains the results of a series of hydrogen-deuterium exchange reactions carried out with a single sample of cycled, unsupported chromic oxide which had been pretreated with hydrogen or oxygen at 500°. The activity for hydrogen-deuterium exchange at -78° was determined in triplicate experiments for both the oxidized and the reduced catalyst, pretreatment and evacuation being at 500°; reasonable reproducibility was obtained. With the oxidized catalyst, evacuated at 500°, equilibrium for hydrogen-deuterium exchange at -78° was attained within four to seven hours (experiments 5, 6, 7), while the reduced catalyst, also evacuated at 500°, required less than ten minutes to reach equilibrium. The exchange proceeded too rapidly on the reduced catalyst to permit study of the kinetics; however, for the oxidized catalyst, the first-order rate constant was in the range 0.5 to 1.0 hour⁻¹ at -78°.

TABLE II

H₂-D₂ EXCHANGE ACTIVITY AT -78 AND -195° AS A FUNCTION OF PRETREATMENT; UNSUPPORTED CHROMIA

Exp. no.	Pretreatment		Temp. of H ₂ -D ₂ exchange, °C.	Activity
	Treated at 500° with	Temp. of evac., °C.		
1, 2, 3	H ₂	500	-78	Equil. (46% HD) within 10 min.
4	H ₂	500	-195	14% HD in 27 hr.
5, 6, 7	O ₂	500	-78	Equil. within 4 to 7 hr.
8	O ₂	500	-195	Inactive
9	O ₂	-78 ^a	-78	Inactive
10	H ₂	-78 ^b	-78	Equil. within 20 min.
11	H ₂	-78 ^b	-195	Inactive
12	H ₂	-195 ^c	-195	Inactive
13	H ₂	500	-195	6% HD in 29.0 hr.

^a Cooled from 500 to -78° in O₂. ^b Cooled from 500 to -78° in H₂. ^c Cooled from 500 to -195° in H₂.

The electrical resistance of the catalyst sample during the oxygen pretreatments at 500° was about 3000 ohms, and it approximately doubled on evacuation at 500°. When, at the conclusion of each exchange experiment, the temperature of the evacuated sample was again raised to 500°, essentially the same resistance was observed as during the initial evacuation.

(8) D. J. Salley, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1131 (1941).

The behavior of the prereduced catalyst was similar (the resistance of the reduced catalyst was 0.5 megohm in hydrogen at 500° and 0.4 megohm after the 16-hour evacuation). To the extent that the oxidation-reduction state is characterized by the resistance, therefore, the low temperature exchange reaction did not affect the preconditioned state of the catalyst. Consistent with this conclusion is the fact that in these experiments the atom per cent. deuterium in the gas phase remained constant, within experimental error, during hydrogen-deuterium exchange at -78° over both oxidized and reduced catalyst. A decrease of 1% in the atom per cent. deuterium in the gas would correspond to an exchange of "catalyst hydrogen" equivalent to about 2% of a monolayer. This failure of "catalyst hydrogen" to participate in the exchange reaction at -78° is very reminiscent of the observation of Kummer and Emmett⁹ that hydrogen adsorbed at higher temperatures on singly promoted iron catalysts did not exchange with deuterium at -195°, although exchange occurred rapidly between gaseous hydrogen and deuterium.

The equilibrium constant, $K = (\text{HD})^2/(\text{H}_2)(\text{D}_2)$, at -78° for the exchange reaction was found to be 2.88 ± 0.01 (based on 44 determinations). This value agrees well with an average value of 2.92 obtained by Gould, Bleakney and Taylor¹⁰ with chromia and nickel catalysts.

As experiment 8 demonstrates, chromic oxide oxygen-treated and evacuated at 500° is not active for hydrogen-deuterium exchange at -195°. In experiment 9 the catalyst was cooled in oxygen to -78° after high temperature treatment, and it was then evacuated for one hour at -78°; presumably some of the adsorbed oxygen which would be desorbed by evacuation at 500° is not removed at -78°. This catalyst was completely inactive even at -78°.

Low temperature evacuation of the 500° hydrogen-treated catalyst left the chromia still able to catalyze the hydrogen-deuterium exchange at -78° (experiment 10), but the ten minute gas sample did not quite correspond to equilibrium; this may represent a difference from the catalyst evacuated at 500°. The catalyst was inactive at -195° after it was cooled in hydrogen from 500° to either -78 or -195° and pumped at those temperatures (experiments 11 and 12). An attempt to measure exchange at -78° on the reduced catalyst, cooled in hydrogen and pumped only at -195°, was dropped when it was found that adsorbed hydrogen was desorbed from the catalyst on warming from -195 to -78°. Experiment 13 was a repeat of 4; the results indicate that the sample had not suffered much loss of activity during the series of experiments.

The chromia-alumina catalyst studied was pretreated with oxygen and hydrogen at 500° in a manner similar to that employed for unsupported chromia, and the catalytic activity was then determined at -78 and -195°. The results are summarized in Table III. Both oxidized and reduced catalysts were very active at -78°. At -195°,

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

(10) A. J. Gould, W. Bleakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

however, the oxidized chromic oxide was completely inactive, while the reduced chromic oxide showed a small, but appreciable activity. These results are qualitatively similar to those obtained for unsupported chromic oxide, the reduced material being more active than the oxidized.

TABLE III

H₂-D₂ EXCHANGE ACTIVITY AT -78 AND -195° AS A FUNCTION OF PRETREATMENT; CHROMIA-ALUMINA

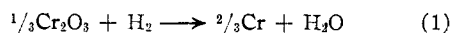
Exp. no.	Treated at ^a 500° with	Temp. of H ₂ -D ₂ exchange, °C.	Activity
14, 15	O ₂	-78	Equil. (46% HD) within 0.5 hr.
16, 17	H ₂	-78	Equil. within 10 min.
18	H ₂	-195	2.4% increase in HD in 25 hr.
19, 20	O ₂	-195	Inactive
21	H ₂	-195	1.1% increase in HD in 31 hr., 2.7% in 74 hr.

^a Catalyst evacuated at 500° after gas treatment at 500°.

Discussion

Most interpretations of the behavior of non-intrinsic oxide semiconductors have been based on the assumption that only slight deviation from stoichiometric composition occurs. Any studies of the influence of the gas atmosphere on electrical properties of semiconductors should be guided by the principle that the gas treatments should not cause gross changes in chemical composition or crystal structure; this is a caution which frequently is overlooked. In the particular case of chromic oxide, it is illuminating to consider the thermodynamics for the reduction and oxidation of the bulk material.

Chromic oxide is quite stable toward reduction.¹¹ For the reactions



and



the standard free energy changes at 800°K. (527°C.) are, approximately, $\Delta F_1^\circ = +24$ kcal., $\Delta F_2^\circ = +16$ kcal. These values correspond to equilibrium constants, $K = p_{\text{H}_2\text{O}}/p_{\text{H}_2}$, of $K_1 = 3 \times 10^{-7}$, $K_2 = 3 \times 10^{-5}$. For a hydrogen partial pressure of 1 atmosphere, therefore, the water partial pressure must exceed 3×10^{-7} atmosphere to prevent reduction to metallic chromium, and must exceed 3×10^{-5} atmosphere to prevent reduction to chromous oxide. Consideration of the water evolved when chromia is cycled in oxygen and hydrogen at high temperature^{12,13} makes it appear likely that this condition was satisfied on the catalyst during the hydrogen pretreatments employed in this work, and no reduction of bulk chromic oxide is to be expected. It may be noted that the stability of chromic oxide toward reduction is even greater at temperatures less than 800°K.

The situation with respect to composition changes on oxidation is more complicated. A variety of oxides intermediate between chromic oxide and chromic anhydride have been observed on controlled

decomposition of chromic anhydride.¹⁴⁻¹⁷ At low temperatures, or at superatmospheric pressure, it is probable that higher oxides such as chromium dioxide or dichromium pentoxide become the most stable phase. In the presence of oxygen at atmospheric pressure, however, chromic oxide appears to be the stable phase at temperatures above about 400°. It may be concluded that no change in bulk composition will occur on treatment with oxygen at atmospheric pressure and 500°. At 350°, however, there is a possibility of change in the bulk phase on oxidation; this may have been a contributing factor to the difficulty in obtaining reproducible results with pretreatments at 350°.

It will be appreciated that this discussion relates to the thermodynamics of the bulk phases, and that the situation may well be different for the surface layer. The point remains, however, that experimental conditions should be so chosen in work of this kind that at least the nature of the *bulk* phase can be unambiguously specified.

Perhaps the outstanding result of these studies is the fact that, as far as hydrogen-deuterium exchange is concerned, chromic oxide has the *lowest* catalytic activity in the state in which it has the *greatest* number of "defects" responsible for electrical conductivity. The hypothesis is untenable, therefore, that a simple and direct parallelism always exists between activity and conductivity. The data presented do not, however, prove the contrary hypotheses that *no* relation exists between the two phenomena. It is conceivable that P-type semiconductors, such as chromia, are most active for oxidative, rather than hydrogenative, reactions when in their most highly conducting state; the converse may be true for N-type semiconductors.

Sites exist in reduced chromia which catalyze the activation of hydrogen. Adsorbed oxygen or adsorbed water (see succeeding paper) may occupy these sites and thereby act as a poison for hydrogen activation. In any event, it seems clear that the surface chemistry of chromia will have to be considered in detail in order to understand the catalytic behavior. Work along these lines will be presented in a subsequent paper.

The relatively high exchange activity reported by Gould, Bleakney and Taylor¹⁰ for chromic oxide at -195° has been verified only under special circumstances. Fresh catalyst, treated with hydrogen at 350°, had an activity comparable with the catalyst of Gould, Bleakney and Taylor; it is noteworthy that they also employed fresh catalyst treated only with hydrogen at 340°. Chromic oxide which has been stabilized by cycling in oxygen and hydrogen at either 350 or 500° is much less active at -195°; this can be due only in part to the approximately fivefold decrease in surface area which occurs on cycling. Stabilized chromia-alumina shows a comparably low activity at -195°, even in the "reduced" condition.

Acknowledgment.—The authors acknowledge

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

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

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

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

(11) (a) F. D. Richardson and J. H. E. Jeffes, *J. Iron Steel Inst. (London)*, **160**, 261 (1948); (b) C. G. Maier, U. S. Bur. Mines Bull. No. 436 (1942).

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

(13) This Laboratory, unpublished results.

with appreciation the permission granted by the Houdry Process Corporation to publish this article. Their thanks are also due to Dr. G. A. Mills for many helpful discussions of the experiments presented here.

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[CONTRIBUTION FROM THE HOUDRY PROCESS CORPORATION]

Effect of Water on the Catalytic Activity of Chromic Oxide

BY STERLING E. VOLTZ AND SOL WELLER

RECEIVED APRIL 27, 1953

Both reduced and oxidized chromic oxide, after evacuation at 500°, are able to absorb considerable amounts of water at very low pressures at 30°. The catalytic activity of reduced chromic oxide for hydrogen-deuterium exchange at -78 and -124° is completely inhibited by adsorbed water corresponding to about 15% of surface coverage. At -195° only about one-half of this amount is required for complete deactivation. A much smaller quantity of water is necessary to poison the oxidized than the reduced catalyst; at -78° complete deactivation results from the adsorption of water sufficient to cover only 2% of the surface.

Introduction

Previous work¹ in this Laboratory has established that the electrical conductivity is low and the catalytic activity for low temperature hydrogen-deuterium exchange is high for reduced chromic oxide, while the reverse behavior is shown by oxidized chromic oxide.

Since water is formed in the oxidation of reduced chromic oxide or the reduction of oxidized chromic oxide, it is important to determine any effect which adsorbed water may have on the catalytic activity of the chromic oxide. This is especially true in view of the possibility that different amounts of water may remain on oxidized or reduced chromic oxide.

The adsorption of water vapor on chromic oxide has been studied by Harbard and King.² Their results showed that the initial adsorption of the water vapor was complete at about 0.1 relative humidity, beyond which point the amount of water vapor adsorbed increased slowly with increasing pressure. Salley, Fehrer and Taylor³ have shown that 0.35 mole of water per mole of chromic oxide can be removed between 300 to 550° from a chromia gel, even after previous evacuation at 300°. Practically all of the water is desorbed below 500°. They also showed that the addition of as little as one mole per cent. water to a heptane charge stock sharply decreased the extent to which dehydrocyclization proceeded over a chromia catalyst.

In this work water adsorption isotherms at 30° have been determined for oxidized and for reduced chromic oxide. The hydrogen-deuterium exchange reaction has also been studied on oxidized and reduced catalysts as a function of the amount of adsorbed water.

Experimental

Materials.—Tank hydrogen was purified by passage over palladized alumina at 250 to 300° and through a silica gel trap at -195°. Tank oxygen was dried by passage through calcium sulfate. Helium was purified by the use of a charcoal trap at -195°. The deuterium (99.5%) was obtained from the Stuart Oxygen Company and used without further purification.

The distilled water employed in these experiments was degassed by repeated freezing and melting under vacuum.

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

(2) E. H. Harbard and A. King, *J. Chem. Soc.*, 19 (1940).

(3) D. J. Salley, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1131 (1941).

The preparation of the unsupported chromic oxide used in this study has been described elsewhere.¹ Prior to use, this catalyst was stabilized by cycling several times in hydrogen and oxygen at 500°; its specific surface area after this treatment was 35 m.²/g.

Apparatus and Procedure.—The water adsorption isotherms were determined in a standard adsorption apparatus⁴ equipped with a water reservoir and an extra gas buret.

The hydrogen-deuterium exchange experiments were carried out in a high vacuum system. An all-glass circulating pump was employed to circulate the reaction mixture over the catalyst, and the sampling system was so designed that small gas samples could be taken for mass spectrographic analyses at any desired time. In most of the experiments the catalyst was treated with hydrogen (or oxygen) at 500° for three hours, evacuated for one hour, re-treated with hydrogen (or oxygen) for three hours, and then evacuated for at least 16 hours. It was then cooled to room temperature under helium and, after the helium was evacuated, the desired amount of water vapor was admitted to the catalyst. The adsorption of water was essentially complete in less than one minute for amounts of water up to about 150 μ moles of water per gram. The catalyst was then cooled to a low temperature and a 50-50 mixture of hydrogen and deuterium was admitted to the reactor.

Results

Water Adsorption.—Figure 1 contains the water adsorption isotherms at 30° for chromic oxide after either oxygen or hydrogen treatment at 500° and evacuation at 500°. In both cases there is an initial adsorption of 140 to 180 μ moles of water per gram catalyst which occurs at very low pressures, after which the adsorption increases gradually with increasing partial pressure. The amount of the initial adsorption corresponds approximately to a third of a monolayer, using 10.8 Å.² as the effective cross-sectional area of an adsorbed water molecule. In the absence of confirming data, no significance is attributed to the slightly higher adsorption values shown by the reduced catalyst.

Effect of Water on Activity of Reduced Chromic Oxide.—In Table I are summarized data showing the influence of water, adsorbed at room temperature, on the catalytic activity of reduced chromic oxide for hydrogen-deuterium exchange at -78, -124 and -195°. Within the limitation of the experimental procedure, adsorbed water exerted no influence on the activity at -78° up to an amount of 35 micromoles per gram; equilibrium was achieved

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