mia.[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) ⇄ (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.

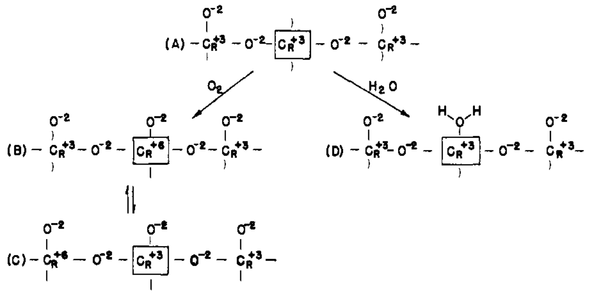

Fig. 5.—Chromic oxide surface (schematic representation).

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MARCUS HOOK, PA.

[29] M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

[CONTRIBUTION FROM THE HOUDRY PROCESS CORP.]

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

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

Experimental

The catalyst employed in this work contains 20% chromia supported on γ-alumina; it is Houdry Type R catalyst, used commercially for butadiene production. The specific surface area of the batch used in this work was 50 m.^{2}/g.

The purification of reagents and the experimental procedures have been described previously.[1,2]

Results

Gas Adsorption.—A number of adsorption isotherms were determined both in a static system and in a circulating system equipped with a cold trap. The results of the 500° isotherms are summarized in Table I. The isotherms were quite flat in the high pressure region; for simplicity, values are given only for the gas adsorbed at about one atmosphere. A comparison of these data with those obtained for unsupported chromia[2] shows that: (1) the reversible oxygen adsorption on the oxidized, evacuated catalyst is about the same for both catalysts; (2) the reversible hydrogen adsorption on chromia is several fold greater than on chromia–alumina; and (3) the total hydrogen taken up by reduced chromia and the total oxygen taken up by oxidized chromia are also several times greater than the corresponding values for chromia–alumina.

TABLE I

HYDROGEN AND OXYGEN ADSORPTION ON CHROMIA–ALUMINA AT 500°

	Static system,[a] μmoles/g.	Circulating system,[a] μmoles/g.
O_2 ads. by oxidized chromia–alumina	21	20
H_2 ads. by reduced chromia–alumina	20	10
O_2 ads. by reduced chromia–alumina	84	115
H_2 ads. by oxidized chromia–alumina	168	245

[a] Catalysts were evacuated for 16 hours between pretreatment and adsorption.

The extent of reduction is dependent on the amount of water vapor present during the reduction; it is greater in the circulating system with "in-line" cold trap, which provides more efficient drying of the gas. The same type of behavior has been observed with unsupported chromic oxide.[2]

Attempts were made to determine the adsorption isotherms at −78° for hydrogen on both oxidized and reduced chromia–alumina (evacuated at 500°). The quantities of hydrogen adsorbed at all pressures were less than the experimental error of the determination. Since this catalyst is very active for hydrogen–deuterium exchange at −78°,[1] it is clear that the occurrence of appreciable amounts of adsorption at this temperature is not a necessary condition for the existence of exchange activity.

Excess Oxygen.—The amounts of excess oxygen on the chromia–alumina as determined by direct iodometric titration are given in Table II.[3] Although the pelleted samples required several hours for all the oxidized chromium to react, as compared with 15 minutes for the ground material, the same *final* value was reached in both cases. The oxidized chromia–alumina contains as much excess oxygen (per gram) as unsupported chromia.[2] If the average value of 0.163 m.^{2} chromia area per micromole excess oxygen (determined from the work on unsupported chromia) is used, a specific chromia area of 22 m.^{2}/g. catalyst is obtained for the chromia–alumina sample. This is 40–45% of the total surface area. The results for reduced chromia–alumina imply that this catalyst contains a small amount of residual excess oxygen. This result is not attributable to inaccessibility of the pellets to hydrogen during reduction, since reduction of ground pellets gave the same value; nor is it attributable to the base alumina, which in a control experiment was essentially without oxidizing power.

TABLE II

EXCESS OXYGEN ON CHROMIA–ALUMINA

Catalyst	Pretreatment at 500°C.	Physical form	Excess oxygen, μmoles/g.
Cr_2O_3-Al_2O_3	O_2	Pelleted	136
		Ground	131
Cr_2O_3-Al_2O_3	H_2	Pelleted	17
		Ground	15
γ-Al_2O_3	O_2	Pelleted	4

Reversible Changes in Cycling.—The weight changes on cycling chromia–alumina in hydrogen and oxygen were studied at 500 and 427°. The catalyst underwent 2.28% weight loss when heated to 500° in nitrogen; this is probably due to the loss of water. The stabilized chromia–alumina gained about 0.1% weight in oxygen and lost the same amount in hydrogen at both 500 and 427°.

The amounts of water evolved by chromia–alumina at 500° in both hydrogen and oxygen were also determined. About 170 micromoles of water per gram is liberated in hydrogen and 90 micromoles per gram in oxygen, for a total of 260 micromoles per gram in a complete cycle.

In order to check the results of Givaudon and coworkers,[4] the thermal effects obtained on cycling chromia–alumina were studied. Results for ten-minute treatments (used by Givaudon) at 500° are similar to those of Givaudon: (1) no deflection occurred during the ten-minute nitrogen flushes employed between exposure to hydrogen or oxygen, (2) the ratio between the thermal effect in hydrogen and that in oxygen was about 3-4:1, and (3) a decrease in the thermal effect occurred on successive cycles. It was then found, however, that if gas treatments of longer duration (0.5 hour or longer) were used, the decrease on successive cycles disappeared. The decrease with ten-minute periods is, therefore, not to be attributed to an intrinsic loss in catalyst activity, but rather to the finite time required for completion of the oxidation or reduction (or for desorption of water).

Similar experiments at 390° showed much lower thermal effects than at 500°. At the lower temperature, a ratio of about 8:1 was obtained for the maximum deflection in hydrogen to that in oxygen.

Discussion

By combining the results of the gas adsorption measurements and the direct iodometric determination of excess oxygen, it is possible to construct a

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(3) The direct method used in this work for determining excess oxygen was found to give about twice as high a value for oxidized chromia–alumina as did the indirect method of Givaudon,[4] with the use of a four-hour Soxhlet extraction period. This casts some doubt on the quantitative validity of Givaudon's results.

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

schematic representation of the surface oxidation–reduction levels; the result is shown in Fig. 1. The levels were computed by the procedure given in a previous paper.[2]

Comparison of Fig. 1 with similar data for unsupported chromia[2] shows that chromia and chromia–alumina differ markedly with respect to the amount of hydrogen adsorbed on the reduced catalyst at high temperature. Whereas unsupported chromia can take up about one hydrogen atom per surface oxide ion, chromia–alumina has a very low capacity for adsorbing hydrogen; in fact, within the experimental error, it cannot be definitely stated that *any* adsorbed hydrogen is retained by reduced chromia–alumina after evacuation at 500°. This might have been adduced as evidence for stabilization of the Cr^{+3} state by the alumina support (since hydrogen adsorption can be considered as equivalent to chromous oxide formation), except for the fact that the amount of excess oxygen taken up by oxidized chromia–alumina is quite comparable with that taken up by unsupported chromia.[2]

The conditions under which the water evolution during cycling in hydrogen and oxygen at 500° was determined are analogous to those employed for gas adsorption in the circulating system. The total amount of water evolved during a complete cycle at 500° was 260 micromoles water per gram; according to part (A) of Fig. 1, the calculated amount would be (2 × 134) + 13 = 281 micromoles water per gram.

The thermal effects observed during cycling chromia–alumina in hydrogen and oxygen at 500° are similar to those previously described for unsupported chromia.[2] In the case of chromia–alumina, however, it would appear that practically all the water should be formed during the reduction, since there is very little adsorbed hydrogen on the reduced catalyst. It must be concluded, therefore, that the heat effects are not exclusively due to the production of water as postulated by Givaudon and co-workers.[4]

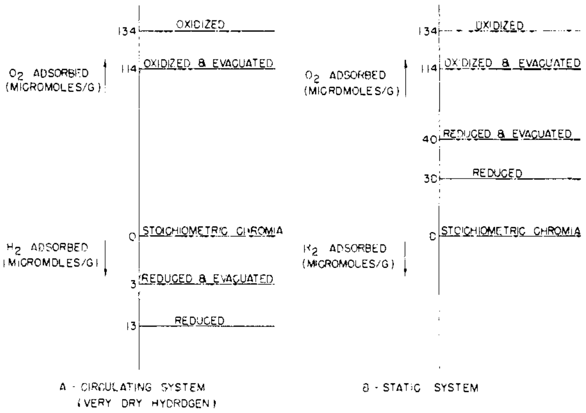

Fig. 1.—Schematic representation of the oxidation–reduction levels of chromia–alumina.

Experiments with unsupported chromia indicated that the excess oxygen present after high temperature oxidation may be used as a rough measure of the specific surface area of the chromia (within, say, a factor of two).[2] To the extent that this procedure is valid, a chromia area of 22 m.²/g. *catalyst* may be calculated for the chromia–alumina (see above). Since only 20% of the catalyst is chromia, the chromia area is 5 × 22 = 110 m.²/g. *chromia*, which is three times the value (35 m.²/g.) obtained for a stabilized, unsupported chromia catalyst; that is, the chromia is three times more efficiently distributed in the supported than in the unsupported catalyst. The equivalent chromia particle diameter in the supported catalyst is 106 Å., as compared with 335 Å. for the unsupported chromia.[3]

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[CONTRIBUTION NO. 138 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Adsorption of Ionic Surfactants and their Gegenions at the Air–Water Interface of Aqueous Solutions

BY C. P. ROE AND P. D. BRASS

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The adsorption of ionic surfactants and their gegenions in the air–water interface of aqueous solutions has been studied by means of surface tension measurements under conditions which permit a simple and exact interpretation. The significant result disclosed is that the surface excess in a surfactant solution does not vary with the concentration of surfactant in the bulk solution throughout a wide range just below the so-called critical micelle concentration. Composition of the adsorbed layer and thermodynamic properties of the dissolved surfactant are discussed. Radioactive tracer measurements on solutions of a labeled surfactant have been found to confirm the conclusions reached from surface tension measurements. A new technique for the direct tracer study of adsorption on solid surfaces is described and some results are presented.

Introduction

The behavior of the fatty acid soaps as surface active materials has been studied by a very great number of investigators. Despite the vast amount of work reported in the literature, there appears to be one aspect of the subject which has escaped attention, namely, the relatively simple and yet exact interpretation of surface tension data available when the hydrogen ion and gegenion concentrations are held constant as the detergent ion concentration is varied in a range below but near to the critical micelle concentration. In the present paper this subject is discussed on the basis of data obtained by two independent absolute methods. The treatment is extended to classes of materials other than the fatty acid soaps.

It is well known that the surface tension of an ionic detergent solution is in general a sensitive