Sites Active for Catalytic Hydrogen–Deuterium Equilibration over α-Chromia

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Abstract: Hydrogen–deuterium equilibration measurements and parahydrogen conversion measurements have been made on powdered ruby, chromia supported on α-alumina at various surface concentrations, and pure α-chromia. Pretreatment conditions have been found for the development of strong catalytic equilibration activity on all samples. The results have been interpreted in terms of surface structure which appears, for this reaction, to involve a dihydroxylated chromium 3+ ion capable of releasing either a proton or molecular hydrogen, with simultaneous reversion to the 5+ oxidation state. The active chromium ion is not directly accessible to molecular hydrogen. The 2+ oxidation state is probably formed under certain conditions, but it does not participate in the hydrogen–deuterium equilibration reaction. Adjacent sites containing chromium are not necessary, but probably contribute to thermal stability. These conclusions are supported by a variety of related studies.

This is the third paper from this laboratory in which there is described an attempt to identify surface structures present on chromia and capable of catalyzing the hydrogen–deuterium equilibration reaction. The first paper[1] showed that ruby (a dilute solid solution of chromia in α-alumina), after treatment in pure flowing hydrogen for 1 hr at 500°, has little more catalytic activity than does α-alumina similarly treated. The ruby, so treated and then cooled to room temperature under conditions such that little chemisorption of hydrogen was possible, showed a remarkable activity for the magnetic process parahydrogen conversion. It also had the ability to chemisorb hydrogen in the 0–400° temperature range.

From these results it was concluded that the activation of hydrogen for the catalytic equilibration reaction requires two or more adjacent sites containing chromium or, alternatively, that the oxidation state produced on the surface of a highly active chromia supported on high-area alumina by hydrogen at 500° is not the same as that produced on ruby. The first hypothesis was examined in the second paper[2] by the study of supported chromia in various cluster sizes on α-alumina. Again it was found that little or no equilibration activity was generated by the pretreatment described. Attention has, therefore, been directed in the present paper to the possibility that hydrogen treatment at 500° may create an inactive surface species on ruby and, depending on conditions, also on chromia supported on α-alumina, but not necessarily on pure α-chromia or on chromia supported on high-area alumina.

The experimental work consisted of parahydrogen conversion rate measurements, hydrogen–deuterium equilibration rate measurements, and various related studies on ruby, on pure α-chromia, and on chromia supported on α-alumina. Pretreatment methods were found for generating strong catalytic equilibration activity over each of these samples. From the results it became possible to exclude certain surface structures and to suggest others that appear probable as contributors to the activity observed.

Experimental Section

Catalyst Preparation. Most of the samples have been described previously.[1,2] Thus, pure α-alumina, ruby, and α-chromia derived from a single crystal and referred to below as α_c-Cr_2O_3 were obtained from Linde Division, Union Carbide Corp. These were crushed in a pure α-alumina mortar and pestle to specific surfaces (BET, N_2) of 2.0, 2.0, and 14.6 m^2, respectively. Criteria of critical purity limits have been described.[1]

A sample of α-chromia, referred to below as α_g-Cr_2O_3, was prepared from chromia gel (obtained by urea hydrolysis of a chromic nitrate solution). The gel was dried and then slowly heated in air to 1100° for 18 hr. The specific surface was about 1.0 m^2, and the X-ray diffraction pattern was that of pure α-Cr_2O_3.

Chromia supported on α-alumina was made by impregnation of the powdered Linde α-alumina (described above) with chromic nitrate solution, followed by drying and ignition at 500°. One sample contained 0.012 wt % Cr_2O_3, another 0.045 wt %.

Reagents. All hydrogen and deuterium gases used were passed through (separate) Engelhard palladium diffusion process purifiers. Helium was passed over hot copper oxide, then over Linde Molecular Sieve 4X at room temperature, then over Sieve 5X at −196°.

Catalytic Activity Measurements. These measurements have already been described.[1,2] In brief, a flow system was used at 50 ml/min over the sample which was placed on a medium porosity fritted Vycor disk. The gas pressure was 1 atm. Criteria of freedom from accidental poisoning (other than that produced by hydrogen) were based on poisoning rate studies at different hydrogen flow rates, as described.[3]

Parahydrogen concentrations were measured in a calibrated Gow-Mac TrIII, W_2, thermal conductivity assembly operating at 60°. Hydrogen–deuterium concentrations were measured in an AEI, MS-10, mass spectrometer. Analyses were accurate for the p-H_2 to about ±1%, and for the H–D to about 0.5%.

Catalyst masses ranged from 1.5 mg to 1.0 g and were chosen, so far as possible, to provide equal total numbers of surface chromium ions in each catalyst sample. This procedure is convenient although obviously very approximate. Rates were selected so that they could readily be compared with that over pure α-alumina. In most cases the reactions were not permitted to go beyond 50% of the distance to equilibrium.

Adsorbed Gas Volumes. An attempt was made to measure the volume of hydrogen necessary to poison a sample of α_g-Cr_2O_3 that had previously been heated in hydrogen at 500° and then cooled to 150°. For this purpose a 1-g sample was used. After all the parahydrogen conversion activity was lost (about 1 hr) the hydrogen was replaced by flowing helium. Subsequently the temperature was rapidly raised to 500°. The exit helium carrying desorbed hydrogen was passed over hot copper oxide and the water so formed was trapped at −196°. Finally, the water was heated and passed through a calibrated thermal conductivity cell at 125°. This procedure gave results reproducible to ±10% of the measured volume of hydrogen.

An attempt was also made to find the volume of oxygen taken up when a 1-g sample of α_g-Cr_2O_3 was heated in oxygen for 20 min at 500° and then cooled to 150°. At this latter temperature the oxygen in the system was replaced by helium, then by hydrogen.

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(1) P. W. Selwood, *J. Am. Chem. Soc.*, **88**, 2676 (1966).

(2) P. W. Selwood, *J. Catal.*, **12**, 263 (1968).

(3) P. W. Selwood, Proceedings of the 4th International Congress on Catalysis, Moscow, 1968, Preprint 66.

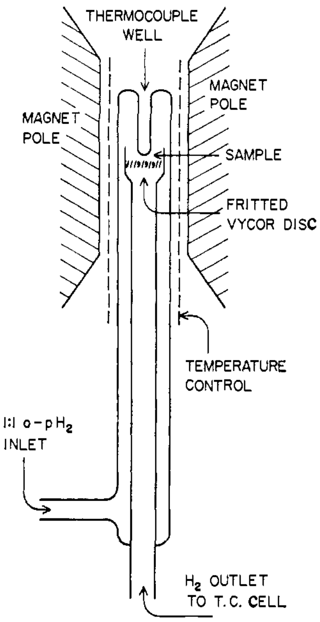

Figure 1. Reactor arrangement for observation of the extrinsic field effect.

The temperature was then raised to 500°. Water formed was first trapped as before and then measured. The hot copper oxide was omitted in this determination. Here again, reproducibility was about $\pm 10\%$ of the oxygen volume taken up by the sample.

Equilibrium Fractional Surface Coverage. An understanding of the complicated thermal decay pattern of the surface species active for hydrogen–deuterium equilibration is aided by some knowledge of the equilibrium fractional surface coverage of the chromia by hydrogen at 1 atm, at various temperatures, after the chromia has received a preliminary treatment in hydrogen at 500°.

In earlier papers[1–3] it was shown that, subsequent to being heated in hydrogen at 500°, ruby and other forms of chromia become poisoned for the magnetic parahydrogen conversion through chemisorption of hydrogen. This hydrogen may be removed by evacuation above about 450°. Alternatively, the chemisorbed hydrogen may be removed by flushing the sample with pure helium, rather than by evacuation. However, the chemisorption of hydrogen proceeds rather slowly, even at 400°. By cooling the sample in hydrogen rapidly, that is to say by quenching it, over the sensitive range from 450 to 150° at a rate not less than 40°/min, it is possible to reach room temperature without having permitted appreciable surface contamination with hydrogen to have occurred. The rate of poisoning at room temperature is sufficiently slow as to permit accurate determination of the parahydrogen conversion rate. It was this method that was used to determine the equilibrium fractional surface coverage of the chromia with hydrogen at temperatures in the range 200–500°.

A 0.5-g sample of ruby containing 1 atom % Cr_2O_3 was held in hydrogen at 550° for 1 hr. The sample was then quenched, as described above, to 25°, after which the parahydrogen conversion rate was measured. This rate was taken to represent zero coverage, with chemisorbed hydrogen, of the species showing magnetic conversion activity, no dissociative activity being present. The experiment was then repeated with the sample being quenched from progressively lower temperatures, and down to 25° in each case for the conversion rate measurement. The time the sample was held at each elevated temperature was guided, as previously reported,[3] by the time necessary to effect a steady state of poisoning by hydrogen. The experiment was repeated with a 15-mg sample of α_g-Cr_2O_3.

Extrinsic Field Effect. In any polycrystalline sample there arises the possibility of surface heterogeneity caused by exposure of different crystallographic faces, but information concerning the relation of these effects to catalytic activity is meager. Although our understanding of the extrinsic field effect[4] is still rudimentary it was thought possible to gain in this way some qualitative insights, and this proved to be correct. The experiment itself will be described in some detail.

The extrinsic field effect is a change in the rate of parahydrogen conversion when the catalyst is placed in a magnetic field. Over chromia in the room temperature region the conversion mechanism is exclusively magnetic and, consequently, it is convenient to refer to the field produced by the paramagnetic ions as the intrinsic field, and that applied from the outside as the extrinsic field.

Pure hydrogen is passed through a converter containing commercial chromia–alumina catalyst at −196° to obtain the 1:1 ortho–parahydrogen mixture. This is then led through a Vycor reactor containing a fritted Vycor medium porosity disk 13 mm in diameter. The disk serves to hold the catalyst. The 1:1 hydrogen mixture passes through the disk and catalyst, as shown in Figure 1, and escapes through a thermal conductivity cell and flow meter. The reference gas side of the cell contains flowing 3:1 hydrogen. Both inlet and outlet sides of the reactor are protected by U-traps at −196°. Gas flow is 30 to 50 ml/min at 1 atm, and appropriate temperature controls are provided from −196 to 800° as may be desired. The reactor is placed between the poles of a 12-in. electromagnet, with homogeneous fields up to 18,000 Oe.

In a typical run a sample of α-chromia was placed in the reactor. The sample was heated to 500° in 1 atm of flowing hydrogen, after which it was quenched, as indicated in the preceding subsection, to the desired temperature. A rate yielding 50% conversion from 1:1 to 3:1 ortho–parahydrogen is convenient for observation of the extrinsic field effect. On application of the extrinsic field a change in rate of conversion was observed. Typical changes ranged from a few per cent to nearly 100% in different samples under various conditions. Over ruby the effect appears always to be positive. Over polycrystalline α-chromia the effect is generally negative below the Néel point (the magnetic phase transition at 34°), and positive above. With increasing extrinsic field the effect tends toward saturation.

With a 15-mg sample of α_g-Cr_2O_3 in the reactor, preheated as above at 500°, the zero field conversion and the extrinsic field acceleration were measured at 23° and also at 45°, these temperatures being selected as slightly lower and slightly higher than the Néel point. At these temperatures the magnetic conversion activity over chromia is slowly poisoned by hydrogen, becoming negligible after about 4 hr. Measurements of the extrinsic field effect were continued until it became too small to observe. Zero field conversion rates were reproducible to about $\pm 1\%$, and fractional rate changes in the extrinsic field to about $\pm 5\%$ until the conversions became quite low.

Results and Inferences

In this section there will be described the results obtained from attempts, by various procedures, to generate catalytic activity for the hydrogen–deuterium equilibration reaction over ruby, over α-chromia, and over chromia supported on α-alumina. In this, and in the following Discussion section, the word "activity" will be used solely for the above dissociative reaction, and not for the magnetic parahydrogen conversion reaction. There will also be described in this section the results of various experiments performed to aid in characterization of the active species. Conclusions that follow logically and obviously from the experimental results are also given in this section.

Preliminary experiments showed that ruby, first heated to 500° in oxygen, cooled, and then heated to about 225° in hydrogen, developed strong catalytic activity. At this stage the identities of the active, and related, species could only be conjectured. Consequently, both active and related species are described in this section solely in terms of pretreatment. For example, a sample of crushed ruby was heated in 1 atm of flowing oxygen at 500° for 1 hr. The oxygen was then replaced by helium at 1 atm and 500° for 1 hr. Then the sample was cooled (at any rate unless otherwise stated) to 25°. The helium was finally replaced by hydrogen. All of the above treatment is condensed to the

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(4) M. Misono and P. W. Selwood, *J. Am. Chem. Soc.*, **90**, 2977 (1968); **91**, 1300 (1969).

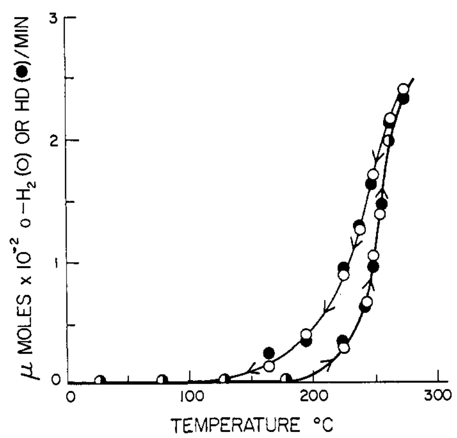

Figure 2. Rate of formation of o-H_2 (O) and of HD (●) over 1 % ruby ($O_2$500He25H_2).

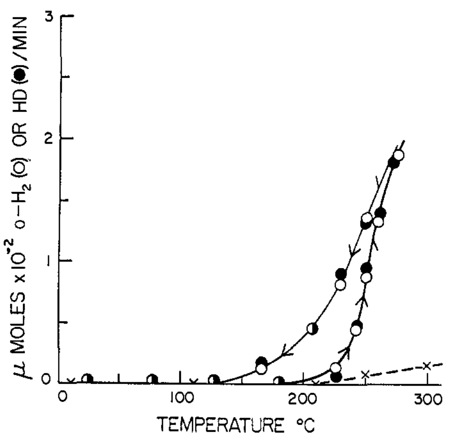

Figure 3. Rate of formation of o-H_2 (O) and of HD (●) over 0.1 % ruby ($O_2$500He25H_2). The parahydrogen rate over this sample treated ($H_2$500q25) is indicated thus (X——X).

formula ($O_2$500He25H_2), and whatever surface species may have been formed is so designated.

As a convenience to the reader of the Discussion section, the several groups of results in each subsection bear letters.

A. **Activity on α-Alumina**. The empty reactor previously heated to 500° in hydrogen, then quenched to 25°, that is to say ($H_2$500q25) showed no measurable activity at 25°, and 17 μmoles of HD/min at 250°. After ($O_2$500He25H_2) the activity was the same within experimental error.

As previously reported[1] it was confirmed that α-alumina, after ($H_2$500q25), showed little more activity than the empty reactor. This, however, rose to 55 μmoles of HD/min (including that of the empty reactor) at 250° after ($O_2$500He25H_2). This is about 20 % of the activity shown by ruby containing 1 atom % Cr_2O_3 under the same conditions and, consequently, it cannot be ignored. All activities reported in the following subsections have been corrected for the activity shown by the empty reactor plus alumina, in applicable cases, such as for ruby and for chromia supported on α-alumina.

B. **Generation of Activity on Ruby**. A 0.5-g sample of powdered ruby ($O_2$500He25H_2), slowly heated, started at about 225° to show an increasingly rapid parahydrogen conversion rate as the temperature continued to rise. After identical treatment the same sample showed almost exactly the same rate of hydrogen–deuterium equilibration. Both of these results are given in Figure 2. Activity during falling (and subsequent) temperature changes was slightly higher, at each temperature, as shown in Figure 2, provided that the maximum temperature reached was not over 250°. There was no measurable activity at room temperature.

From the above result it may be concluded that the active species is generated by hydrogen in the neighborhood of 200°, as previously shown for chromia gel by Burwell[5] and others. But this "activation" of the ruby occurs only if the ruby has received a "preactivation" heat treatment in oxygen.

C. **Effect of Chromia Concentration in Ruby**. A sample of powdered ruby containing only 0.1 atom % Cr_2O_3, and treated ($O_2$500He25H_2) showed activity as given in Figure 3. While the activity was less, per unit mass, than that shown by 1 % ruby, it is two or three times more active per accessible chromium ion. As the concentration of Cr–Cr ion pairs in ruby may be estimated approximately from the law of mass action,[1] it may be concluded that such pairs are not required for catalytic activity.

D. **Minimum O_2 Preactivation Temperature**. The activation of ruby by hydrogen above 225°, as shown in Figures 2 and 3, did not occur unless the sample had been pretreated in oxygen at elevated temperature. The minimum temperature at which oxygen preactivation occurred was found approximately by taking samples, previously treated ($H_2$500), then heated in oxygen at progressively higher temperatures, before the final activation in hydrogen at 225°. Thus a 0.5-g sample of 1 % ruby treated ($H_2$500He25$O_2$130He25H_2) showed, even at 250°, no measurable activity. The same was true for ($H_2$500He$O_2$220He25H_2), but ($H_2$500-He25$O_2$275He25H_2) gave virtually the same strong equilibration rate shown in Figure 2. From this result it follows that generation of the active site probably does not require an intermediate stage in which the chromium is hexavalent.

E. **Effect of Preadsorbed H_2**. As previously shown,[1] ruby ($H_2$500q25) is poisoned for the magnetic parahydrogen conversion by the chemisorption of hydrogen that occurs slowly at room temperature, more rapidly as the temperature is raised, and that is not readily reversed below 450°. The following experiment was performed to determine if the activity generated in ruby by (O_2>275He25H_2) depends on whether the ruby surface is effectively bare, or whether it has been poisoned by hydrogen. At the stage represented by ($H_2$500He25) ruby very strongly catalyzes the parahydrogen conversion, but this is solely by the magnetic mechanism. It was assumed that the chromium ions at this stage were directly accessible to molecular hydrogen.

A sample of 1 % ruby was treated ($H_2$500He25$H_2$275). After 1 hr this sample had lost all its parahydrogen conversion activity, as measured at 25°. All magnetic sites were, therefore, assumed to be inaccessible to molecular hydrogen at this stage. The preparation was now continued by (25He$O_2$275He25H_2), and this sample was found to have almost the same (dissociative) activity above 225° as that shown in Figure 2. The conclusion is, therefore, that prepoisoning by hydrogen has

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(5) R. L. Burwell, A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *J. Amer. Chem. Soc.*, **82**, 6272 (1960).

no ultimate effect on the oxygen preactivation and the hydrogen activation steps subsequently performed.

F. Are the Active Sites Magnetic? The failure (shown in Figures 2 and 3) of powdered ruby (O$_2$500-He25H$_2$) to show any parahydrogen conversion at room temperature permits us to reach the conclusion that at this stage of pretreatment the surface has no paramagnetic sites readily accessible to molecular hydrogen. (The implications of this will be discussed later.) Of more importance is the question: does the active species, after activation has been continued (H$_2$ > 225), now contain any such accessible paramagnetic sites? The near equality of parahydrogen conversion and hydrogen–deuterium equilibration shown in Figure 2 for the active species at 250° is evidence that no important magnetic mechanism contributes to the former. Further evidence was provided by the following series of results.

First, 0.5 g of ruby (O$_2$500He25H$_2$), showing strong equilibration activity at 250°, was quenched in hydrogen to 25°. The sample then showed no activity of any kind. But this negative result is inconclusive because nothing is known concerning the rate and mode of chemisorption of hydrogen on the active sites.

Second, the same sample, reactivated, was flushed at 250° with helium, then cooled to 25° before hydrogen was readmitted, namely (O$_2$500He25H$_2$250He25). This product was also free of any kind of activity at 25°. But this negative result still leaves some residue of uncertainty, because dissociative activity may involve sites that, at 250°, are nearly all covered with hydrogen.

The third, and final, experiment in this group was to sweep the active species at 250° with helium (as in the second experiment) but then to raise the temperature to 500° for 20 min prior to cooling, in helium, to 25°. Hydrogen was then readmitted, but this species (O$_2$500-He25H$_2$250He500$\rightarrow$25H$_2$) was free of any kind of activity.

From the above results it may be concluded that the active species (for H–D equilibration) has no appreciable concentration of paramagnetic surface sites directly accessible to molecular hydrogen. The possibility that heating the active species in helium might destroy its activity was easily eliminated by going through the preparative sequence (O$_2$>275He25H$_2$255He500$\rightarrow$250H$_2$). This product had lost no activity as compared with the original active species.

G. Thermal Decay of Activity. Above about 275° the active species on ruby begins to decay in hydrogen. Thus, above 275° the continuing rapid rise of activity with increasing temperature is no longer virtually exponential. At 300° the decay is readily observable over a period of hours. Interest in the mechanism and products of this obviously reductive decay process lies in the possibility that they may give some clue to the structure of the active species.

For a 0.5-g sample of ruby (O$_2$>275He25H$_2$) the parahydrogen conversion rate (clearly dissociative) at 300° was 229 μmoles of o-H$_2$/min. The initial decay rate was 0.67 μmole/min^2. At 350° the initial conversion rate was decaying too rapidly for accurate measurement but, at about 475 μmoles/min, was obviously approaching equilibrium conversion. At this temperature the decay rate was 5.6 μmoles/min^2. At 425° the decay rate was very rapid but a small residue of, presumably, dissociative activity survived a few minutes of heating in hydrogen at 500°.

The same sample of catalyst under identical conditions gave a hydrogen–deuterium equilibration rate of 215 μmoles of HD/min at 300°, and an initial decay rate at this temperature of about 0.6 μmole/min^2. It may, therefore, be concluded that, at least during its initial stages, the decay process is essentially a loss of dissociative activity, without appreciable contribution from a magnetic conversion. (This further confirms the statements made, in subsection F, concerning the absence of magnetic sites in the dissociatively active species.)

If the continuing decay of dissociative activity with time was measured by hydrogen–deuterium equilibration it was found that the rate of equilibration fell more or less logarithmically to zero, with a half-life ranging from minutes to days, depending on the temperature. At 300° the half-life was several hours. At no time during the decay process did the sample show any activity as measured at room temperature.

But if the decay was measured by parahydrogen conversion the results were more complicated. Conversion rate decay below 300° resembled that for equilibration rate decay, with the final result being complete, or almost complete, lack of activity of any kind below 300°. On the other hand, decay rate as monitored by parahydrogen above about 350° slowly decreased and reached zero, giving a conversion rate that was dependent on decay temperature. Thus, for decay measured at 300° the final, steady-state, conversion at 300° was near zero. For decay at 350° the final conversion rate was less than half the initial rate, and for decay at 400° the final rate was well over half the initial rate. Furthermore, as decay proceeded at these somewhat elevated temperatures it was found that the temperature coefficient of total activity gradually changed sign, becoming negative as the time necessary for complete decay of the equilibration activity was approached.

At the end of a period long enough to destroy all the equilibration activity it was found that only magnetic conversion activity remained, and this generally has a negative temperature coefficient, except where rapid desorption of a catalyst poison may confuse the situation. The magnetic conversion so generated was found also to undergo poisoning by hydrogen at the same rates, and with the same induction period, followed by straight-line decay, as previously reported[1,3] for ruby (H$_2$500q25).

The implication is clear thatru by (O$_2$>275He25H$_2$ >300) becomes identical with ruby (H$_2$500q25) after sufficient time has elapsed for decay of the dissociatively active species to become complete. Final confirmation that (O$_2$>300He25H$_2$>300) gradually becomes identical with (H$_2$500He25H$_2$) was obtained by the sequence (O$_2$>300He25H$_2$>300He500$\rightarrow$25). This product had the same rate of parahydrogen conversion at 25° as did (H$_2$500He25).

The relation of these results to the equilibrium surface coverage, with hydrogen, of (H$_2$500q25) at various temperatures will be mentioned in subsection K.

H. Pure α-Chromia. It has often been noted that alumina (H$_2$500q25) shows varying degrees of dissociative catalytic activity, depending on the crystallinity of the sample. As α-Cr$_2$O$_3$ and α-Al$_2$O$_3$ are isostructural, it is not surprising that the former was found to show some transitory dissociative activity after ($H_2$500q25). Fortunately, this proved to be relatively small and it decayed fairly rapidly. Proper timing of activity measurements rendered this complication negligible.

Previous work showed that α_c-Cr_2O_3 (derived from a single crystal) had a surprisingly low conversion activity after ($H_2$500q25). A 1.5-mg sample treated (O_2-300He25H_2) showed only 72 μmoles of HD formed/min at 250°, and it was suspected that oxygen preactivation might require a higher temperature than had been found sufficient for ruby. This proved to be the case, and ($O_2$500He25H_2) showed an activity of 307 μmoles/min at 250°. However, because of the uncertainties concerning the low magnetic conversion rate on this sample (initially prepared from the melt), further work on this sample was abandoned in favor of α_g-Cr_2O_3, namely, α-Cr_2O_3 derived from chromia gel by ignition.

A 3.0-mg sample of α_g-Cr_2O_3 showed neither magnetic nor dissociative activity at 25° after ($O_2$500He-25H_2). The α_g-Cr_2O_3 is, therefore, like ruby in presenting no paramagnetic species directly accessible to molecular hydrogen after this treatment; but above 200° the dissociative activity began to rise, and reached 275 μmoles of HD/min at 250°. This sample then showed measurable dissociative activity at room temperature, thus proving that hydrogen above 200° does indeed have an "activating" function, as has been pointed out by others for more conventional chromia catalysts.

When the above sample was subsequently treated ($H_2$500) it lost part of its dissociative activity, but nevertheless remained active for a long time at 250°, thus showing that, unlike ruby, pure α-Cr_2O_3 may be "activated" by hydrogen alone, without the "preactivation" by oxygen required for ruby.

The same sample of α-Cr_2O_3 treated ($H_2$500q25) showed no dissociative activity at 25° although it did show, as expected, a strong magnetic conversion activity. This magnetic activity decayed by an approximately straight line mechanism with a half-life of about 2 hr at 25°. If, after poisoning of the magnetic activity was complete, the temperature was raised, a slow rise of dissociative activity was observed. Cooling of the sample from 500° yielded, as above, a dissociative activity of 150 μmoles of HD/min at 250°. This remained unchanged over many hours.

It may be stated, on the basis of the above results, that the magnetic sites of α-Cr_2O_3 are able to function independently of the dissociative sites, if both are present. It may also be stated that complete poisoning of the magnetic sites, as must occur fairly rapidly at 250° (Figure 4), does not interfere with the dissociative activity. In other words, magnetic and dissociative sites may be present on this catalyst simultaneously; but, taking the results of this subsection together with those of subsection F, it is seen that no appreciable fraction of sites may provide both functions simultaneously, unless the temperature is considerably higher than 250°. There is no reason to doubt that a given chromium ion may act as a key structural feature in both kinds of sites, given the pretreatment appropriate to the generation of each kind of site.

I. Supported Chromia. The results on chromia supported on α-alumina are of interest because they represent one further step toward the more familiar, highly active, chromia supported on high-area alumina. The new data will be summarized.

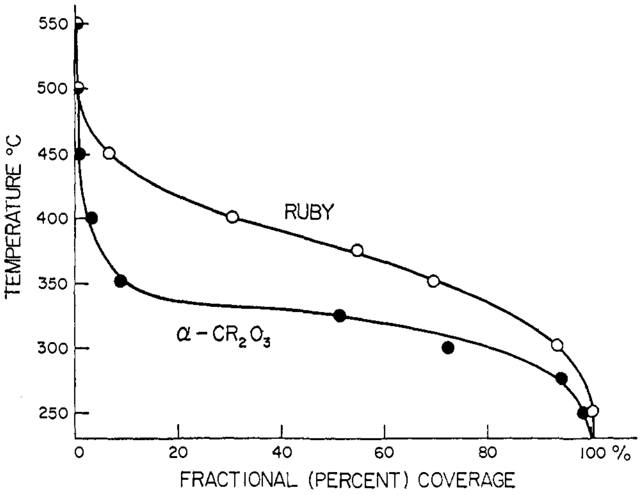

Figure 4. Fractional surface coverage with hydrogen at equilibrium, at the indicated temperature, for ruby and for α-chromia.

A 0.5-g supported sample containing 0.045 wt % Cr_2O_3, and treated ($H_2$500q25), showed no dissociative activity at 25° after the usual 1 hr of heating at 500°, but it did show a small but measurable activity at 250° if the heating at 500° was interrupted after 10 min. The same sample treated ($O_2$500He25H_2) showed an extremely high activity at 250°, with clear indication that some "activation" process had occurred in the 200–225° region. This sample then showed measurable activity at room temperature.

A 0.5-g supported sample containing 0.012 wt % Cr_2O_3 showed no activity up to 300° after ($H_2$500q25), but a very strong and remarkably stable activity at 225° after ($O_2$500He25H_2).

These supported samples, containing quite different chromia cluster sizes, as previously reported,[2] are seen to behave catalytically, and to be responsive to pretreatment, in manners intermediate between ruby and pure α-chromia. As expected, the more dilute supported sample resembled ruby in requiring oxygen preactivation. The more concentrated sample gave a modified indication of activity if the oxygen pretreatment was omitted. The probable reasons for this behavior will be taken up in the Discussion section.

J. Chemisorbed H_2 and O_2. A 1-g sample of α_g-Cr_2O_3 treated ($H_2$500He150) and allowed to stand 1 hr yielded a blank determination of 3 μl of H_2 when heated rapidly to 500° in flowing helium. The same sample treated ($H_2$500q150) and allowed to stand 1 hr, to the completion of conversion activity poisoning, yielded 55 μl (STP) of H_2.

The corrected volume of hydrogen chemisorbed during ($H_2$500q150) to complete poisoning is then 1.5×10^{18} molecules. As the specific surface of the sample is about 1 m^2 it may be estimated,[3] very approximately, that there are 3×10^{18} chromium ions accessible to the hydrogen. MacIver and Tobin[6] give about 9.8×10^{18} ions for the (001) exposed plane. This gives an atom ratio of H/Cr = 1, in fair agreement with that previously reported for ruby,[3] and for supported chromia

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(6) D. S. MacIver and H. H. Tobin, *J. Phys. Chem.*, **64**, 451 (1960).

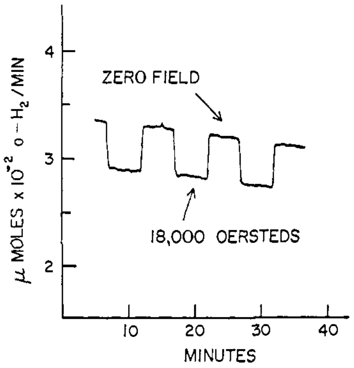


Figure 5. Rate of formation of o-H_2 over α-chromia ($H_2$500q25) with application of a magnetic field to the catalyst for 5 min out of every 10.

on α-alumina.[2] However, it must be emphasized that the large probable error in estimating the number of chromium ions on the surfaces of the samples makes it impossible to do more than to say that H/Cr = 1, in all cases, within a factor of 2 or 3.

A 1-g sample of α_g-Cr_2O_3 treated ($O_2$500→150He) then heated in hydrogen to 500° yielded a corrected volume corresponding to H/Cr = 11. Here again the accuracy cannot be claimed to be better than by a factor of 2 or 3. But, as reduction of Cr^{6+} down to Cr^{2+} would require that H/Cr = 4, it may be concluded that ($O_2$500) for 1 hr oxidizes all, or nearly all, of the surface to Cr^{6+}, or that partial oxidation involves some chromium ions below the surface. Under these circumstances it was somewhat surprising to observe that the α_g-Cr_2O_3 remained a bright green during and after ($O_2$500). It may further be noted that owing to the widely different experimental conditions it is not surprising that these results bear little relation to those of MacIver and Tobin.[6]

K. Equilibrium Fractional Surface Coverage. Figure 4 shows the equilibrium fractional surface coverage of ($H_2$500) with hydrogen as a function of temperature. As described in the Experimental Section, the time the sample was held in 1 atm of hydrogen at each temperature (t) was that necessary to reach a steady state of conversion activity. The horizontal axis is $1 - (r_t/r_{550})$ where r_t is the initial parahydrogen conversion rate at 25° *after* the sample had been quenched from temperature t, and r_{550} is the initial rate for the, presumably, bare surface after the sample had been quenched from 550°. (Success of this method depends, of course, entirely on the slowness of hydrogen chemisorption on ($H_2$500) at room temperature.)

Measurements are reported for ruby and for α_g-Cr_2O_3, after pretreatment ($H_2$500). It will be noted that coverage is complete for both samples for $t < 250°$, but that ruby holds the hydrogen somewhat more tenaciously at more elevated temperatures. This may be related to the dissociative activity shown (subsection H) by α-Cr_2O_3, and not by ruby, above 250° after the indicated pretreatment.

It will be noted that the results shown in Figure 4 aid in the understanding of the complicated thermal decay patterns of dissociative activity described in subsection G. If decay in hydrogen is followed at only moderately elevated temperatures, the magnetic sites generated will be poisoned by hydrogen as soon as they are formed; but at somewhat higher temperatures a fraction of these sites will remain bare and thus active for magnetic conversion.

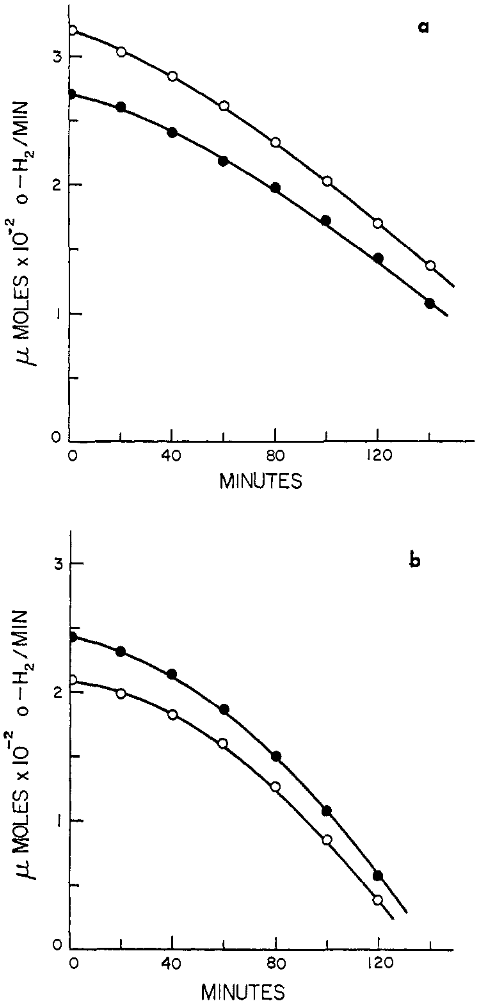


Figure 6. Extrinsic field effect in 18 kOe (●) during H_2 poisoning at (a) 23° and (b) 45°.

L. Extrinsic Field Effect. No previous results of the extrinsic field effect as a function of catalyst surface poisoning have been published. For that reason there is given in Figure 5 a portion of the recorder chart showing parahydrogen conversion rate *vs.* time for a 15-mg sample of α_g-Cr_2O_3 ($H_2$500q25). A field of 18,000 Oe was applied to the catalyst for 5 min out of every 10-min period. The run was made at 23°, at which temperature the change of rate on application of the field is negative. It will be noted that the change of rate occurs very quickly after the field is applied or removed. The change is recorded as soon as the hydrogen flowing at 50 ml/min has had time (about 2 min) to reach the thermal conductivity cell. The start of catalyst poisoning may also be observed in Figure 5.

Figure 6 shows μmoles of o-H_2 formed per min until poisoning approaches completion. Runs are shown at 23 and 45°, these temperatures being respectively 11° below, and above, the Néel point. Extrinsic field accelerations were observed at 18,000 Oe. Note that the effect changes sign at the Néel point (34°), and also that the zero field conversion rate diminishes rather sharply as the temperature rises through the Néel point.[4]

Figure 7 shows fractional extrinsic field accelerations as a function of accessible surface during poisoning by hydrogen. In this case the vertical axis is the fractional change of conversion rate in 18,000 Oe at time T, the horizontal axis is $1 - (r_T/r_0)$ where r_0 is the initial conversion rate in zero field and r_T is the conversion rate at time T in zero field. The extrinsic field effect is measured essentially as a differential effect (extrinsic field on and off), and consequently the precision of the measurements is somewhat greater than might be surmised by inspection of Figure 6.

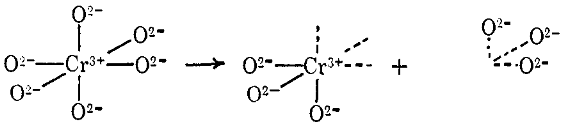
The extrinsic field effect measurements show that the acceleration observed in the field is almost independent of surface poisoning. The implications of this will be discussed in the following section.

Discussion

This section will be devoted to consideration of models consistent with the experimental facts developed in preceding sections or, where applicable, already known from earlier work. First, the most important experimental facts will be restated in concise form. 1. Catalytic activity for the hydrogen–deuterium equilibration reaction is generated on chromia by an "activation" in hydrogen in the 200–225° temperature range. (Burwell, *et al.*,[5] and others; also subsections B and H.) 2. Over ruby, activity is not developed unless there has been a "preactivation" in oxygen above 275° (subsections B and D). 3. Heating the active species above 275° in hydrogen diminishes dissociative activity, with formation of a species capable of strongly catalyzing the magnetic parahydrogen conversion, but also subject to partial, or complete, poisoning by hydrogen below 450° (subsection G). 4. The active site contains no paramagnetic species directly accessible to molecular hydrogen (subsection F). 5. The active species is not restricted to the presence of chromium ions in clusters (subsection C).

The discussion will start with the active sites on ruby, in which chromium–chromium interactions are negligible. Presumably this means that sites on ruby active for the dissociation of molecular hydrogen are not necessarily adjacent to each other, or, if they are adjacent, only one of every pair need contain a chromium ion.

For each octahedral site containing, in ruby, a Cr^{3+} or Al^{3+}, or remaining vacant, crystal fracture may result in the loss of one, two, or three oxide ions. The last possibility, resulting from fracture in the plane of a close-packed layer, is the most convenient to consider first, and it is quite possibly the most probable mode of fracture. (The meager evidence on this point will be considered later.) The site containing Cr^{3+} thus becomes a surface site with an exposed Cr^{3+}, and an opposing surface with an exposed vacancy.



Cr site prior to fracture

Cr site (A3) after fracture

vacancy site (B3) after fracture

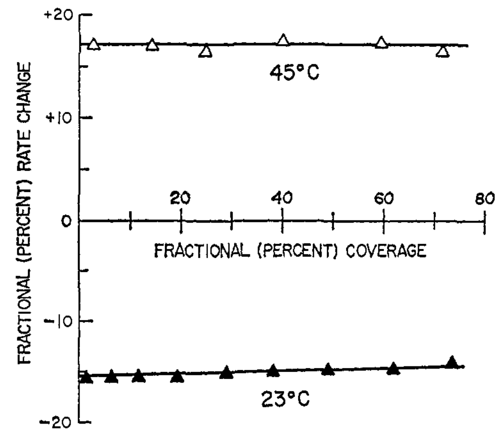


Figure 7. Extrinsic field effect in 18 kOe, during H_2 poisoning, as a function of surface coverage at 23° and at 45°.

The possibility suggested by Davis[7] that movement of oxide ions on the surface may partially obscure the Cr^{3+} ions cannot be ignored, but the experimental results of Weller and Voltz,[8] and the high magnetic conversion rate reported in the present paper, render this possibility less likely.

The site A3 has 1.5 excess positive charges, and site B3 1.5 excess negative. Local electrical neutrality may be achieved in several ways, of which, for our purposes, the adsorption of charged species is the most important. This, however, may not actually be necessary, because any cation-containing site adjacent to site A3 could become a vacancy site corresponding to B3. Thus, local neutrality could readily be achieved without the introduction of any foreign species. It will, therefore, be considered that site A3 is the starting point for the discussion, although it is obvious that no such site could long exist unchanged in anything less than an ultra high vacuum.

Arguments similar to that above show that the loss, in fracture, of two oxide ions from an octahedral site containing Cr^{3+} would yield A2 sites having −0.5 excess charge. This could be neutralized if an adjacent Al^{3+} (in ruby) should go to the opposite fracture face. Neutralization could also be achieved in this case by Cr^{3+} becoming Cr^{4+}, the extra +0.5 charge then being shared with an adjacent A2 site containing Al^{3+} rather than Cr^{3+}.

Finally, fracture involving the loss of only one oxide ion from a Cr^{3+} site would yield A1 with −2.5 excess charges neutralized by transfer of an adjacent Al^{3+} to the opposite fracture face.

The reaction of sites A3, A2, and A1 with adsorbed molecules will now be considered. The gases are oxygen and hydrogen. It may be pointed out that A3 sites possess this unique property of being able to adsorb one molecule (or ion) symmetrically in tetrahedral coordination, or, alternatively, up to three molecules or ions, of appropriate size, to restore the original octahedral coordination. These possibilities may play a part in the development of catalytic activity on the ruby surface. The tetrahedral coordination of Cr^{6+} as an active species in olefin polymerization by chromia has already been established by van Reijen and Cossee.[9]

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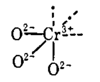
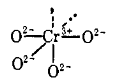
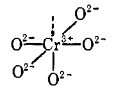
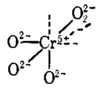
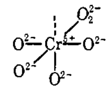
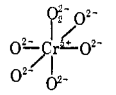
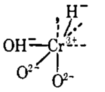
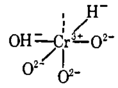
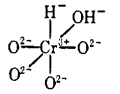
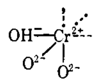
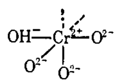
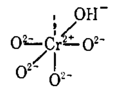
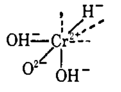
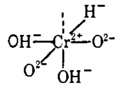
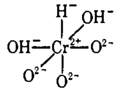
(7) R. J. Davis, "Chemisorption," W. E. Garner, Ed., Academic Press, New York, N. Y., 1957, p 230.

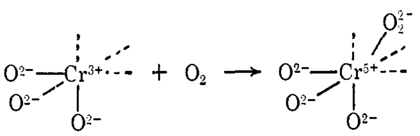
(8) S. W. Weller and S. E. Voltz, *J. Am. Chem. Soc.*, 76, 4695 (1954).

(9) L. L. van Reijen and P. Cossee, *Discussions Faraday Soc.*, 277 (1966).

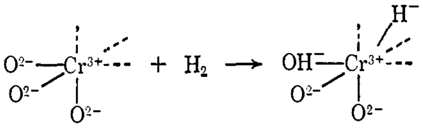
Table I. Some Possible Primary Adsorption Complexes

Species no.	Adsorbate	A3	A2	A1
I	(Virgin)			
II	Oxidative O_2			
III	Heterolytic H_2			
IV	Reductive H_2			
V	Hetero-reductive H_2			

Let us consider the virgin site A3 exposed to molecular oxygen. A possible mode of chemisorption is as follows



the peroxide ion being at an apex of the tetrahedron so formed. Similarly, the interaction of a site A3 with molecular hydrogen could be represented



In Table I there are shown various kinds of adsorbent–adsorbate complexes formed by virgin sites A3, A2, and A1 with molecular oxygen and hydrogen. Secondary interactions between adsorption complexes and hydrogen, when they appear to be related to dissociative activity, are considered later. Many possibilities, other than those presented, will suggest themselves; justificationf for some of the choices follow. Steric considerations make some of the examples improbable.

Various authors consider the virgin state of chromia surface to be one in which the Cr^{3+} ions are not directly accessible to adsorbate molecules, but are rather covered with a close-packed layer of oxide ions. It is difficult to see how this could be true of samples created by fracture along a close-packed layer. Each such layer has Cr^{3+} ions between it and the two adjacent oxide ion layers. Furthermore, the initial parahydrogen magnetic conversion rate[1-3] on ruby and other samples after treatment ($H_2$500q25) is about 100-fold greater (per unit mass of chromia on the surface) than any previously reported. In fact, the activity is about the maximum predicted theoretically by Leffler[10] for such a case. This certainly suggests that the paramagnetic ions, after this pretreatment, are directly accessible to molecular hydrogen.

Another question may be raised concerning the choice of peroxide ion as the illustrative ligand for ruby treated with molecular oxygen at moderately elevated temperatures. The possible formation of superoxide ion, O_2^-, or of any other paramagnetic surface species in such a case appears to be excluded by the lack of any magnetic parahydrogen conversion activity after such exposure (subsection F). The direct formation of an oxide ion as the ligand appears improbable because of the lack of a four-electron reducing mechanism at any site on ruby.

Species in Table I involving only one hydrogen atom are included because of the virtual certainty that hydrogen may migrate on the surface of alumina.[3,11,12]

It may also be pointed out that almost all practical solid catalysts involve, at some stage, a condensation from solution of the potentially active species. (Few industrial chemists prepare catalysts from single crystals.) Because of this, the ligands such as water, oxygen, etc., are generally already in position in the coordination sphere. The usual methods of describing generation of the active site are, therefore, quite different from that given here.

Turning now to the species that may take a direct part in dissociative catalytic activity, we see that the ability of ruby to show such activity permits, for the moment, elimination from consideration of those species involving two or more chromiums adjacent to each other (subsection C). The first essential step is a "preactivation" in oxygen above about 275° (subsections B and D). While the exact configuration at this stage is not critically important for our purposes, it clearly involves a state of oxidation higher than Cr^{3+}. A similar oxidative procedure has repeatedly[9,13] been shown to be necessary for olefin polymerization over chromia, and the effect of this has been attributed to sites containing Cr^{6+}. Voevodskii[14] has reported a similar requirement for ethylene hydrogenation over chromia gel. The con-

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(10) A. J. Leffler, *J. Chem. Phys.*, **43**, 4410 (1965).

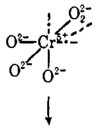
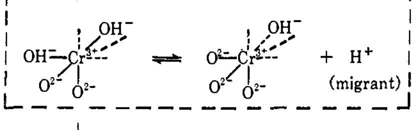
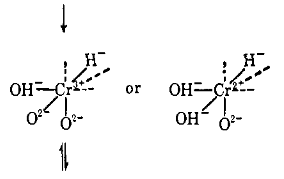
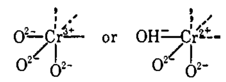
(11) S. Khoobiar, *J. Phys. Chem.*, **68**, 411 (1964).

(12) E. J. Nowak and R. M. Koros, *J. Catal.*, **7**, 50 (1967).

(13) D. E. O'Reilly and D. C. MacIver, *J. Phys. Chem.*, **66**, 276 (1962).

(14) L. A. Shapovalova, L. V. Bryukhovetskaya, and V. V. Voevodskii, *Kinetika i Kataliz*, **8**, 1314 (1967).

Table II. Proposed Formation and Decay of the Active Species on Ruby

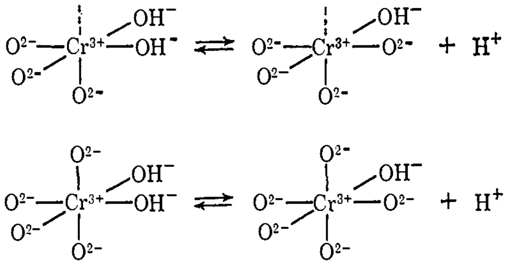
Preparation	Species	Activity
(O_2>275)		None
($H_2$225)		Dissociative precursor
(H_2>200)		Dissociative
(H_2>275<450)		None
(H_2>450)		Magnetic

figuration II (A3) in Table I appears possible for this species.

Before it shows activity for the hydrogen–deuterium equilibration reaction the oxidized species must be "activated" at about 225° (subsection B). There is abundant evidence in the literature[5] supporting the necessity for this step, which clearly suggests some mild reduction, yielding perhaps, in the case of ruby, O^{2-} instead of $O_2{}^{2-}$, but certainly not Cr^{2+}. At this stage the sample becomes highly active for the equilibration reaction in the 200–275° region (subsection B). Through this stage no species shows appreciable parahydrogen conversion activity unless equilibration activity is also present. There is no evidence that any paramagnetic species is both present and directly accessible to molecular hydrogen (subsection F).

If the active species is heated above 275° in hydrogen, the dissociative activity is destroyed (subsection G). The product then exhibits a strong magnetic conversion activity, provided that poisoning by hydrogen can be prevented. Reference to Figure 4 shows that, unless the temperature is moderately high, poisoning will be complete and, above 200°, fairly rapid. But above about 450° the surface will be free of chemisorbed hydrogen over the magnetic species. If then quenched, or cooled in helium or under vacuum, it will show the magnetic conversion activity previously reported.[1] This magnetically active species must certainly contain chromium ions in an oxidation state considerably lower than 6+, and these sites must also be directly accessible to molecular hydrogen. Reference to Table I shows that the magnetic species could be I (A3) or IV (A3). The hydrogen-poisoned species could be III (A3) or V (A3). Numerous authors have suggested that the treatment ($H_2$500) of chromia yields Cr^{2+}, or at least that the average surface oxidation state is less than 3+. It seems to the writer that while this is probably true, it is doubtful whether hydrogen at 275° would suffice for this reduction. The matter is discussed by Shelef, Otto, and Gandhi.[15]

Possible configurations derived from A3 fracture, for the formation and reductive decay of the active species on ruby, are shown in Table II. For those sites in which the chromium ion has lost two, or only one (A2 and A1), of its octahedrally coordinated O^{2-} ions, representation of the active species may be formulated similarly.



The only important difference in these two cases, as compared with those derived from the A3 virgin site, is that the tetrahedrally coordinated adsorbate ion is neither possible nor necessary for steric blocking of the magnetic conversion subsequent to the oxygen "preactivation" step.

The active species for hydrogen–deuterium equilibration is thus seen to be probably a partially hydroxylated chromium 3+ ion capable of reversible release of a proton to the contiguous surface. The problem of accounting for the equilibration reaction on a site containing only one chromium ion is solved because the migrant hydrogen is able to travel over the surface until it reaches a chromium that has become involved with a deuterium rather than a protium molecule. Chromia in the form of ruby owes its ability to chemisorb molecular hydrogen to its variable oxidation state. Alu-

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(15) M. Shelef, K. Otto, and H. Gandhi, *J. Catal.*, **12**, 361 (1968).

mina, which is, under similar conditions, a very poor catalyst by comparison with chromia, possesses this ability to chemisorb hydrogen to a far less degree, although it shares with chromia the Brönsted acidity necessary to transmit hydrogen over the catalyst surface. It will be noted that the steady-state concentration of the hydroxylated chromia species may be quite small. The steps involved when the chromia is actually functioning as a catalyst are shown in Table II.

Evidence favoring these structures and mechanisms will now be summarized and commented upon. It has been shown that there is an oxidation state lower than that of the dissociatively active site. This lower state is dissociatively inactive. It may be concluded that, if 2+ chromium exists under any of these circumstances, it is not important for dissociative activity in the systems described.

The dissociatively active site does not contain a paramagnetic ion directly accessible to molecular hydrogen. This appears to mean that there is no exposed chromium ion present. Heterolytically chemisorbed hydrogen, as an important functional part of the dissociative species, appears, therefore, to be eliminated because it would almost certainly require an appreciable fraction of the chromium ions to be exposed, whatever their oxidation state. This, however, does not change the probability that hydride ion is the chief factor in the hydrogen poisoning which occurs on species treated ($H_2$500q25), which may contain Cr^{2+}. But the hydrogen chemisorbed by ($H_2$500q25) is taken up far too slowly[3] to account for the observed activity of the active species. By contrast, there is ample evidence in the literature that Cr^{5+} is formed under the "preactivation" conditions used here, and that much of this state can survive mild treatment with hydrogen.

We turn now to pure α-chromia. A sample derived from a single crystal showed a large dissociative activity at 250° after oxygen "preactivation" at 500°. However, it is not clear why this sample (derived from the melt) showed such a low magnetic conversion activity after being quenched from 500° in hydrogen.[1] Most attention was, therefore, directed to α-chromia derived from chromia gel. This showed a magnetic activity, after ($H_2$500q25), resembling that of ruby (except for the mechanism of the decay process in hydrogen), and it showed a strong dissociative activity at 250° after "preactivation" in oxygen at 500°. This sample also showed appreciable dissociative activity after treatment with hydrogen at 500°, and this was true even after sufficient time had elapsed for decay of the transitory activity generated in both α-Cr_2O_3 and α-Al_2O_3 by this treatment.

The only important difference between ruby and α-Cr_2O_3 is thus seen to be that appreciable dissociative activity may be generated in the latter without recourse to the oxygen "preactivation." It is not difficult to fit this difference into the model proposed for the activation of ruby. The essential structural difference between ruby and α-Cr_2O_3 is that in the former nearly all the nearer metal ion neighbors of any Cr^{3+} ion are Al^{3+}, while in α-Cr_2O_3 they are Cr^{3+}. Interaction of any kind between Cr^{3+} and Cr^{3+} in ruby is then almost negligible, and the experiments on 0.1% ruby show that for the purposes of this work they are completely negligible. But for the case of α-Cr_2O_3 the situation is quite different. It seems quite probable that a Cr^{2+} ion formed on the surface of ruby would have to remain as such until an oxidizing adsorbate molecule arrived. Stoichiometric α-Cr_2O_3 is, of course, an insulator. But as soon as an alterion, such as Cr^{2+}, is placed on, or generated on, the surface, the sample becomes semiconducting. Electron transfer between the surface Cr^{2+} and an adjacent Cr^{3+} situated below the surface could restore the surface to the 3+ state. This process could continue so long as two oxidation states remained in appreciable concentration on, or in, the sample particle. The process is not limited to Cr^{2+}–Cr^{3+} interaction.

The idea presented in the preceding paragraph may help to resolve some of the ambiguities surrounding the concept of average surface oxidation state as compared with average (bulk) oxidation state.[15] The average surface oxidation state can have a definite meaning in relation to the chromium ions on the surface of ruby. But a meaning in reference to a surface such as that of α-Cr_2O_3 is valid only in terms of the particular experimental method used for the determination. Thus it might, under reducing conditions, be possible to imagine an average surface oxidation state much lower, or about the same, as the average (bulk) oxidation state; and this situation could persist until bulk stoichiometry was approached. This would depend on the semiconductivity and hence on the temperature and other conditions.

The model proposed for dissociative activity in α-Cr_2O_3 is, therefore, exactly the same as that presented for ruby. The migrant proton rarely has, in the case of α-Cr_2O_3, the necessity of traveling farther than to the next adjacent oxide ion. Some further support for these views is found in the results (subsections H and F) in which it is shown that, while there is no reason to doubt that magnetic and dissociative sites may be interconverted, no site functions as both magnetic and dissociative simultaneously on α-Cr_2O_3. There seems ample evidence that both magnetic and dissociative sites may be present simultaneously.

The results on chromia supported on α-alumina fall into the patterns between those of ruby and α-chromia, depending on the surface concentration of chromia (subsection I). At the lower chromia concentration most of the chromia has been estimated[2] as being present in clusters, but these are only three or four atom layers thick. At the higher concentration nearly all the chromia is in clusters, but the fraction of Cr^{3+} on the surface of these clusters is still very large compared with that for the pure α-Cr_2O_3. There is, at first glance, a contradiction in that for the supported samples nearly all the activity is lost after ($H_2$500q25). The reason for this is probably that, owing to the very small size of the clusters they, like the isolated chromium ions on the surface of ruby, are readily reduced to stoichiometric Cr^{2+}, at which stage dissociative activity is lost, although magnetic activity becomes very high.

It might be expected that quantitative measurements of hydrogen and oxygen adsorption on the several chromia preparations would confirm the validity of the species shown in Tables I and II. However, partly from the nature of the samples and partly because of the ambiguities involved in the concept of average oxidation state, the adsorption measurements are not very accurate. The only case in which the problem is not obscured by complications is for the pretreatment ($H_2$500-q25) which becomes completely poisoned for the magnetic conversion over a period of hours or minutes, depending on the temperature. For ruby and for α-chromia the H/Cr ratio on the surface after this poisoning (monitored by conversion rate measurements) is about unity, but it could be 2, or even 3 (subsection J). All that can be said is that the adsorption data are not inconsistent with the species shown in Table II (H/Cr = 2) for this pretreatment. In this connection it has to be stated that there is no real assurance for H/Cr on ruby being the same as for α-chromia. For ruby the possibility of atoms beneath the surface entering into, or complicating, surface reactivity may be remote. But for α-chromia we have the complication referred to above, namely the semiconductivity that is present under conditions of reactivity. Furthermore, the extrinsic field effect (subsection L) appears to offer proof that a bulk physical change can strongly affect purely surface interactions.

Much the same difficulty applies to the oxygen adsorption in the "preactivation" step (subsection J). Here again, all that can be said is that the H/Cr ratio involved in removing the chemisorbed oxygen is high, but not inconsistent with complete oxidation of the surface chromium to the chromate state, as has been shown by many authors. (The problem of how to provide a four-electron mechanism for molecular oxygen chemisorption does not arise on α-chromia, as it does for the isolated chromium in ruby.)

Throughout this discussion it has been implied that the most probable mode by which chromium ions in α-chromia, or in ruby, are exposed on fracture is that involving the loss of three oxide ions from the original octahedron so as to obtain the virgin surface site designated I (A3) in Table I. The reason for this has been partly intuitive,[16] but it is based in part on the surprisingly large magnetic conversion rate shown by all samples after the treatment ($H_2$500q25). A chromium ion that had lost three of its nearest oxide ion neighbors would presumably be more readily accessible to molecular hydrogen than an ion that had lost only one or two oxide ions.

It now appears that evidence in favor of the loss of three oxide ions is at hand in the extrinsic field experiment (subsection L). In the present primitive stage of our understanding of the extrinsic field effect it is not possible to do more than put this matter in qualitative terms. There is in the literature substantial evidence that different crystallographic faces of metals and oxides show different rates and heats of adsorption, for a variety of adsorbates.[17] It may, therefore, be conjectured that fracture of any oxide so as to expose different crystallographic faces would produce a heterogeneity for chemisorption processes, so long as the several faces were exposed in comparable surface proportions.

In α-chromia below the Néel point, as in many other oxides of transition metals, the magnetic susceptibilities are very different along different crystallographic axes, and they are different as measured parallel or perpendicular to the applied magnetic field. In the powder systems studied in the present work, the parahydrogen molecule has, presumably, access (if not equal access) to all exposed faces; and these faces are arranged substantially at random with respect to the applied field. The magnetic moment that is measured by parahydrogen conversion in a powder system is thus an average.

If one crystallographic face adsorbs hydrogen more rapidly than another, then as poisoning proceeds on that face its contribution to the overall conversion rate could diminish more rapidly than the average. But if now, as seems inevitable, the extrinsic field acceleration on that face is different from that on other faces, then there should be observed a change of fractional acceleration as catalyst poisoning proceeds. But, as shown in Figure 7, little such change was observed. It appears, then, that surface heterogeneity of the kind described, as associated with different crystallographic faces, is not an important factor in the powder conversion rate. This, in turn, suggests that one face is dominant. Our choice of the face indicated is based on the very high initial, zero-field, conversion rate observed.

This work, although involving chromia in several forms, was all done on samples permitting quite accurate characterization so far as composition, crystal structure, and particle size were concerned. The principal conclusions were as follows: 1. There is an oxidation state lower than that of the site active for hydrogen–deuterium equilibration. That lower site is inactive. It is, therefore, unlikely that the active site involves chromium in the 2+ oxidation state. 2. If the active site contains chromium (as seems certain) then that chromium ion is not directly accessible to molecular hydrogen. 3. The transitory intermediate active site appears to be a partially hydroxylated Cr^{3+} in tetrahedral configuration, with a higher oxidation state possible.

Comparing Cr^{3+} ions isolated from each other, as in ruby, with supported Cr^{3+} ions in clusters, and with pure α-Cr_2O_3, one finds that the isolated ions may, by appropriate pretreatment, be made as active as any. Supported chromia in clusters possesses the well-known practical advantages of flexibility in preparation and long life. It is to be noted that the possible interactions of the active agent with the support involve an order of complexity that was not considered in this work.

There have been so many suggestions and hypotheses concerning sites of catalytic activity in transition metal oxides that it is impossible to trace where credit is due. No claim for originality with respect to any species mentioned is intended in this paper, but some popular ideas have been eliminated. It must also be pointed out that catalytic properties are often sensitive to what seem to be trivial, even subtle, changes in pretreatment. Because of this, the conclusions reached in the present paper may not be extrapolated to other systems, high-area supports, gels, other pretreatments, and other reactants without extreme caution and reservations.

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